

VAN BRUNT

Reactions during Water Treatment

Chemistry

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1908

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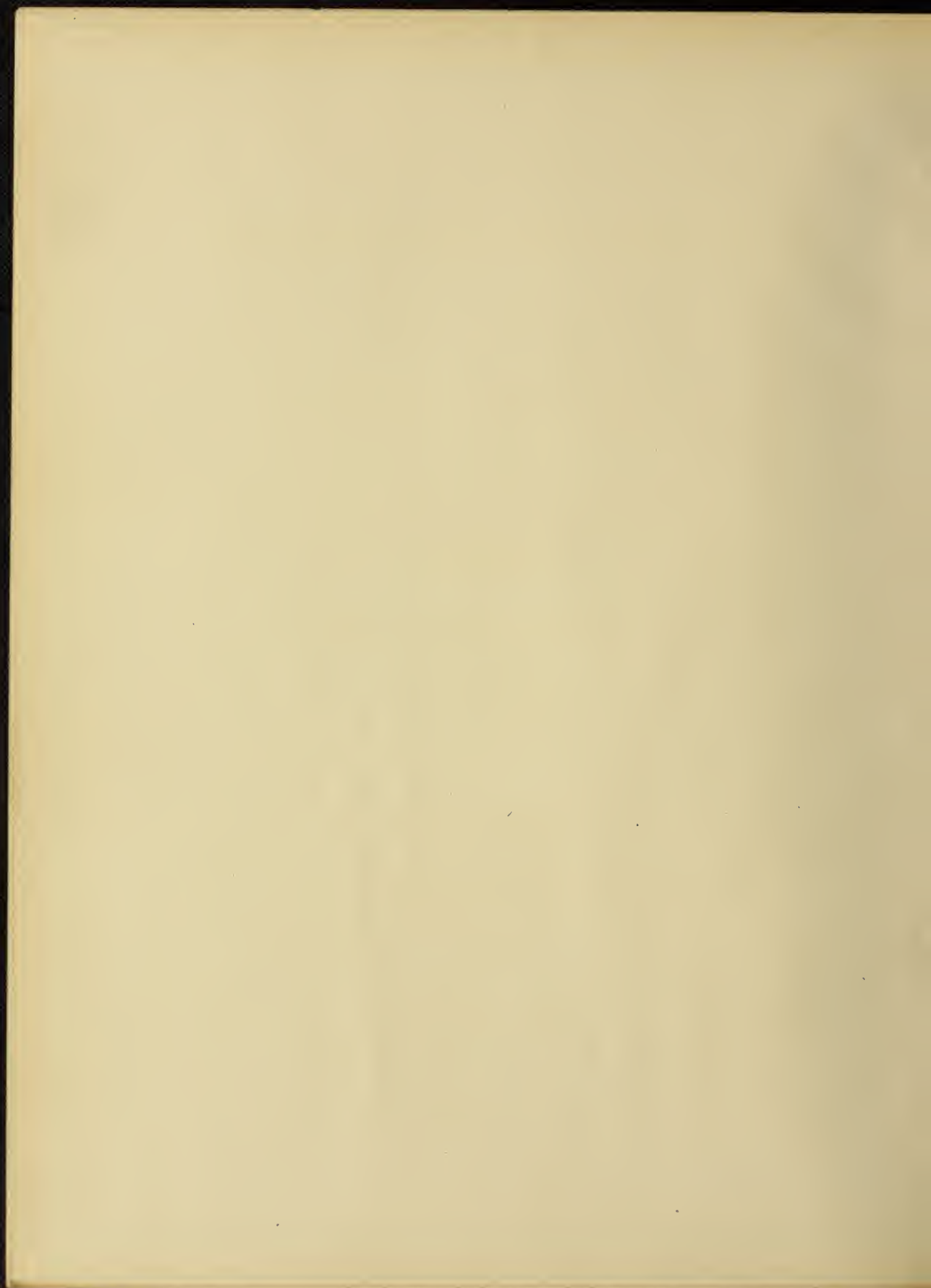
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REACTIONS DURING WATER TREATMENT

BY

GEORGE ATHOL VAN BRUNT

THESIS

For the Degree of Bachelor of Science

in Chemistry

College of Science

University of Illinois

PRESENTED JUNE, 1908

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

George Athol Van Brunt

ENTITLED REACTIONS DURING WATER TREATMENT

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science

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Chemistry

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INTRODUCTION.

The benefit obtained by softening water to be used in boilers and for manufacturing purposes has been known for many years. In the first part of the eighteenth century Thomas Henry proposed to soften water by means of lime.*

*Archbutt & Deely J. S. C. I. 10-511.

In 1841 Clark patented a method for softening water, also by means of lime. His method is to determine the alkalinity, free caustic alkalinity and hardness, then to add the calculated amount of lime.

Porter* took out the first patent on the filtration of water and made the softening process continuous.

*J.S.C.I. Vol. 3. 1884 p 51.

At the sugar refinery of James Duncan in 1884 the Clark-Porter process was given a practical test on a large scale. Later, other manufactures and railroads made more or less extended use of it.

The next advance in water softening was when McNabb and Beckett* discovered that caustic soda, or lime, and soda

*J. S. C. I. 5-267.

ash must be used, if all Magnesium is to be removed. Hereto-

fore only lime alone or soda ash alone had been used.

Macadam* mentions the use of sodium phosphate

*J. S. C. I. Vol. 3-12.

but does not state the reactions and properties.

Archbutt and Deely* published a paper in 1891 in

*J. S. C. I. 10-511.

which they claimed to be the first to use soda ash and lime on a large scale for water softening.

Soda ash and lime, either alone or combined and both with and without the action of heat, are the most widely used softeners at the present time.

The apparatus used varies in the details, but the general principle provides an arrangement for the addition of the chemicals, to the water, in proper proportions.

When we speak of softening a water we mean removing as completely as possible all salts and compounds which consume soap. This embraces the soluble salts of Calcium, Magnesium, Iron and Aluminium. These elements occur principally as Carbonates, Bicarbonates, Sulphates, Chlorides and Nitrates.

It must not be thought that these are the only salts which cause trouble in boilers. Large amounts of Sodium and Potassium salts render a water unfit for boiler use. These

The first part of the paper is devoted to a general
discussion of the problem. It is shown that the
problem is equivalent to the problem of finding
the minimum of a certain function. This function
is defined by the following expression:
$$F(x) = \frac{1}{2} \int_0^1 (x(t) - y(t))^2 dt$$

where $x(t)$ and $y(t)$ are functions of t . The
problem is then reduced to the problem of finding
the minimum of this function. It is shown that
the minimum is attained when $x(t) = y(t)$.
The second part of the paper is devoted to a
detailed study of the problem. It is shown that
the problem is equivalent to the problem of finding
the minimum of a certain function. This function
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salts can only be removed by distillation. Barium, Silica and the Halogens may, and do, occur in waters and must be taken account of in softening. Waters containing large amounts of organic matter and wastes are bothersome as are also waters containing fats, oils and grease. Of course, waters containing appreciable quantities of acids as sulphuric, hydrochloric, nitric or carbonic exert a deleterious corrosive effect on the boiler.

Several things make the softening of water desirable.

1. Action on boilers.
2. Action on soap.
3. Trouble from scaling, clogging, pitting etc.

The action of water on boilers falls under these heads.

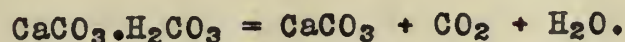
1. Incrusting.
2. Corroding.
3. Foaming and Priming.

There are three general classes of water causing incrustation.

1. Waters containing carbonates of Calcium, Magnesium, etc., generally present as Bicarbonates.
2. Waters containing the Sulphates of these.
3. Waters containing both Carbonates and Sulphates.

When Sodium Carbonate is present in a water of the first class, a soft scale or sludge is formed, which is easily

blown off. If no Sodium Carbonate is present, the Bicarbonates of Magnesium and Calcium lose Carbon Dioxide on heating and a more or less soft scale is formed.



Waters of the second class are precipitated by heat and pressure and form a very hard scale. Other elements if present in such a water may play quite an important part in the formation of scale, as for example Silica, Iron and aluminium, and its character may be greatly changed.

The third class of waters are precipitated, as the previous classes, by heat and form a scale which is hard or soft according as a large or small amount of Sulphates are present.

2. Corrosion means, as its name indicates, a reaction of some constituents of water with the metal of the boiler whereby the metal is eaten away, generally more or less irregularly, giving rise to pits and holes. Christie usually ascribes corrosion to one or other of these causes.

1. Fatty acids from decomposition of animal or vegetable matter.

2. Hydrochloric acid from decomposition of Magnesium Chloride at high temperatures.

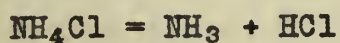
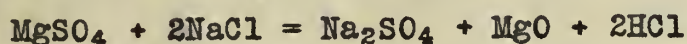
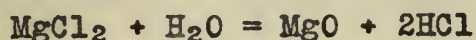
3. Galvanic action.

4. Use of salt.

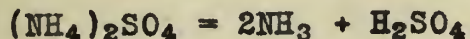
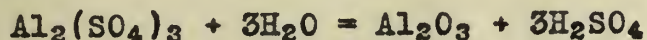
5. Carbonic acid in waters.

Lubricating oils are broken down in the boilers into the fatty acid and glycerine, when the acid forms the corresponding Iron soap by attacking the boiler.

Magnesium Chloride, Sodium Chloride and Iron Chloride in a water may be decomposed giving free acid as follows:



Sulphuric acid is also formed in boilers by decomposition of Sulphates.



Galvanic action in a boiler is not thoroughly understood. It is generally supposed to be due to the interaction of some electrolyte in the water and the boiler plates whereby an electric current is produced. A current of electricity is produced when two dissimilar metals are allowed to touch, in the presence of moisture. Thus, boilers with copper ferrules on the ends of the tubes have been badly corroded. Sheets of Zinc placed in a boiler lessen galvanic action and also the formation of scale on the plates, very much.

A seemingly pure water often proves to be very corrosive, due to the presence of Carbon Dioxide. Christi*

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*Boiler Waters, p. 88.

mentions the case of water which has been formed by heavy snowfalls and says that such water almost invariably causes bad corrosion, if used in a boiler free from scale, due to the presence of Carbon Dioxide. If rain water has absorbed acid, vapors or gases, it will cause corrosion.

Wrought iron corrodes less than steel.*

*Andrews, Inst. C. E. Vol. 77-323.

Manganese in steel increases its tendency to corrode.*

*Inst. C. E. Vol. 88. 28.

Alloys of K, Na, Ba, Al, Mg, Ag, Pt, Sb, As with Iron corrode more rapidly than pure Iron; alloys with Ni, Co, Sn, Cu, Hg and Cr, are less rapidly attacked, the effect varying in each case in the order named.

3. Christi* says, "Foaming is the result of sus-

*Boiler Waters P 117.

pending impurities in the water which rise to its surface in a more or less dirty condition and form a scum." Salts of Sodium and Potassium cause foaming. Experiments have been made to determine the amount of sodium and potassium salts

which were required to produce foaming. The results show that 300 to 400 grains of these salts per gallon will cause foaming. It is hastened by the presence of small suspended particles and also by the presence of other salts. Foaming is dangerous because water is carried over into engines etc., and it also prevents the height of the water in the boiler being accurately known, thus making explosions possible. Furthermore large quantities of fuel and water are wasted.

Priming, according to Christi*, takes place when

*Boiler Waters, P. 117.

water is carried, as steam bubbles, with the steam, up through the water and thus affects the entire depth of water in a boiler.

Tatlock and Thomas*, deny that Carbonate of Sodium

*J. S. C. I. 1903, Vol.23, 428.

has a tendency to produce priming, as has been stated. Sodium sulphate has also been thought to cause priming but they claim it does not do so. They have worked along these lines and in proof of their statements show that one water was used in a boiler until it was sufficiently concentrated to contain 776 grains Sodium Sulphate per gallon and 949 grains Sodium Carbonate, but yet showed no tendency to prime. They conclude that in the positive statements which have thus far appeared regarding priming all the factors have not been considered,

and that priming has been erroneously ascribed to Sodium Carbonate and Sodium Sulphate, and, further that it is impossible to accurately foretell from an analysis whether a water will prime or not.

Scale is a serious hindrance to the longlife and efficiency of a boiler. Several factors go to make this up.

1. The efficiency of a boiler is greatly reduced thus causing much loss of fuel. This loss of efficiency is very hard to determine accurately for any but a specific case. The best way to determine it is to operate a boiler under precisely the same conditions first with, then without scale. Experiments made at the University of Illinois, by the Mechanical Engineering Department, showed that the loss in efficiency due to a scale $3/64$ " thick was 9.55%.*

*L. P. Breckenridge, R. R. Gazette, Vol. 31, p. 60.

2. The scale forms an insulating coating on the plates and hinders the transmission of heat whereby the temperature of the plates is greatly raised. This causes undue strains due to the unequal temperatures, and burns the plates out. Thus the boiler is greatly weakened and serious accidents may take place.

The losses occasioned by the above mentioned effects of scale are increased by, (1) The cost of cleaning out the boilers, pipes, etc., (2) Losses of fuel in heating up boilers which have had to be allowed to cool down for cleaning, (3)

Loss due to the investment in spare boilers to be used when the others are being cleaned.

In industrial uses a hard water is a distinct hindrance. In laundry work a pure water is especially desirable, owing to the fact that a hard water will decompose large quantities of soap, which is not only a great loss, but a dirty scum is formed from the insoluble Calcium soap.

In the household also, a hard water is an undesirable thing. Besides consuming soap and rendering washing harder as mentioned above, it also interferes in cooking as, for example, when albuminous foods are boiled in a hard water, insoluble compounds of Calcium and Albumin are formed and precipitated. Even in making tea and coffee the salts present in a hard water prevent solution of the tea and coffee. A hard water also coats all kettles and pipes heavily.

In brewing a hard water gives much trouble by clogging the coolers or by imparting undesirable tastes to the brew, in either case necessitating distillation.

There are various ways of treating water to soften it. The methods employed and apparatus used depend on the type of water to be softened, amount of chemicals required, etc. It will be well to give, first, some consideration to the mechanical side of water treatment and the various systems and apparatus in general use.

There are two types of water softening apparatus, the intermittent and the continuous. In the intermittent system

two or more treating and settling tanks are required, with a tank for mixing the chemicals, and the necessary stirring devices. The treating tanks are alternately filled with water; the reagents used for softening are added while the tank is being filled with the untreated water, the whole being thoroughly mixed by paddle wheels meanwhile. Thus the raw water and reagents are thoroughly mixed and the sludge from preceeding purifications is stirred up and hastens the re-action, also causing the precipitate to ^{subside} very quickly on standing. After the tank is filled up, the paddle is stopped and the water allowed to stand, to allow the precipitate to settle out. The softened water is then drawn off by some suitable device, allowing as little sludge as possible to be drawn off. The water is then, ordinarily, filtered. While one tank is being filled and treated the other is giving a supply of treated water. By the time it is empty the other is ready for use. The intermittent system has the following advantages. (1) Very accurate treatment may be given a water since a measured amount of water is treated and the exact amount of reagents to produce the best result can be easily weighed out; (2) It is easily adjusted to meet any changes in quality or quantity of water used; (3) The water stands long enough for the reaction to be quite complete, then it can settle; (4) Filters last much longer since only a comparatively small amount of sludge gets on to them; (5) Such an apparatus is very simple, is easily controlled and does not require much space, being

easily fitted into any odd space.

The continuous system may comprise the following parts; a tank having fixed and adjustable weirs or valves; lime slaking tank; lime saturator, or the lime may be added as an emulsion when a considerable quantity is required; lime reactions tank; Soda solution ^{tanks} to be used when Sulphates of Calcium and Magnesium are present ~~and reaction tanks~~; ^{and} settling tank, mechanical gravity or pressure filters.

The water first flows into the weir tank, where it is divided into two parts; the main supply goes through the fixed weir into the lime reaction tank, a smaller quantity flows through an adjustable weir into the saturating tank, where it displaces its own volume of saturated lime water into the water coming from the weir tank into the lime reaction tank. Sometimes the lime solution is made independently and the required amount added by means of float valves.

When the reaction with lime is complete the water flows into the Soda tank, if the treatment with lime alone is not sufficient, where it is treated with Soda solution. It then flows into a settling tank and from thence through a filter. The following advantages may be claimed for the continuous system; (1) Automatic operation. (2) Reaction with one reagent is complete before the other is added, making adjustments easier. (3) Quantity of reagents easily adjusted to varying quality of water. (4) Water is supplied only at rate needed.

THE HISTORY OF THE
CITY OF BOSTON
FROM THE FIRST SETTLEMENT
TO THE PRESENT TIME
IN TWO VOLUMES
BY NATHANIEL BENTLEY
OF THE BARRISTER AT LAW
IN GREAT BRITAIN
AND OF THE CHURCH OF ENGLAND
IN THE UNITED STATES OF AMERICA
LONDON: PRINTED BY J. JOHNSON, ST. PAUL'S CHURCH-YARD, 1786.
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The treatment of water for purification consists essentially in adding some reagent or reagents which will combine with the objectionable salts present in the water and form insoluble compounds which will be precipitated. It may also consist in adding a substance to prevent precipitation in a boiler, or to neutralize acids or substances that will cause corrosion, or to prevent foaming. The objectionable salts are usually the acid carbonates or normal carbonates of Magnesium and Calcium. The sulphates, chlorides or nitrates of these metals and of Iron and Aluminium may also be present.

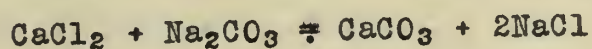
The reagent most widely used is lime. It is used as the oxide, the solid hydrate, Ca(OH)_2 , or as a paste, milk of lime, or even as a saturated water solution. Lime, Ca(OH)_2 , reacts with the bicarbonates of all metals except the alkalies. With bicarbonate of Calcium, $\text{CaCO}_3 \cdot \text{H}_2\text{CO}_3$, in which form Calcium frequently exists in water, it reacts and forms the normal carbonate which is insoluble $\text{CaCO}_3 \cdot \text{H}_2\text{CO}_3 + \text{Ca(OH)}_2 = 2\text{CaCO}_3 + 2\text{H}_2\text{O}$. It has no effect on Calcium Sulphate or Calcium Chloride.

Magnesium when present as the bicarbonate is precipitated thus; $\text{MgCO}_3 \cdot \text{H}_2\text{CO}_3 + 2\text{Ca(OH)}_2 = \text{Mg(OH)}_2 + 2\text{CaCO}_3 + \text{H}_2\text{O}$. Magnesium is also often present as chloride or sulphate, when the following reaction takes place;

$\text{MgCl}_2 + \text{Ca(OH)}_2 = \text{Mg(OH)}_2 + \text{CaCl}_2$ the Mg(OH)_2 is insoluble and comes down as a precipitate but the Calcium Chloride is very soluble and stays in solution leaving as many molecules of incrusting material as was present in the beginning merely

changing Magnesium to Calcium. The same thing takes place when the Magnesium is present as **sulphate**, Calcium sulphate remaining in solution. Thus it is seen that nothing is gained by treating a water containing Magnesium Chloride or Calcium Chloride with lime with a view to removing these substances. Magnesium is removed but Calcium takes its place. Conclusion; lime treatment is only effective in waters which contain bicarbonates of Calcium and Magnesium. It reacts with other salt, of Calcium except the bicarbonates. It reacts with all salts of Magnesium but does not help matters any since an equivalent amount of Calcium goes into solution.

Soda ash is essentially Sodium Carbonate and is used quite extensively for softening water, most frequently perhaps in conjunction with lime. It reacts with $\text{CaCO}_3 \cdot \text{H}_2\text{CO}_3$ to form the normal carbonate of Calcium and Sodium bicarbonate HNaCO_3 . $\text{H}_2\text{CO}_3 + \text{Na}_2\text{CO}_3 = \text{CaCO}_3 + 2\text{HNaCO}_3$. In this case it is inferior to lime as the latter adds no mineral matter to the treated water. The Sodium Carbonate though harmless in small quantities increases the tendency to foam. When Calcium is present as the chloride or sulphate these reactions take place;



thus in both cases the Calcium is removed and a comparatively harmless sodium salt, as mentioned above, is left in solution.

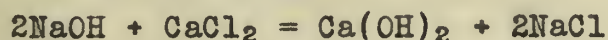
Soda ash does not react with $\text{MgCO}_3 \cdot \text{H}_2\text{CO}_3$ or at most it forms the normal carbonate which is also quite soluble. With the sulphate or chloride of Magnesium, it furnishes

sodium ions to correspond to the acid ions forming MgCO_3 . Conclusion; soda ash is effective in removing the salts of Calcium. It removes all of them, precipitating the Calcium and leaving a harmless sodium salt in solution. It reacts with mineral acid Magnesium salts forming the carbonate which may be removed by lime.

Lime and soda ash are very frequently used together and thus supplement each other. This method of treatment is ordinarily the cheapest and best, since nearly all incrusting and scaling salts are removed. Lime and soda ash are both very cheap and can be obtained almost any where in quantity. Lime costs about $1/2$ ¢ per pound. Soda ash costs about $1\ 1/4$ ¢ per pound. They are also easy to handle.

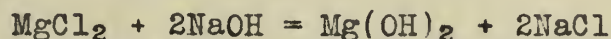
Sodium hydrate, NaOH , is an excellent reagent for softening purposes. It reacts with $\text{CaCO}_3 \cdot \text{H}_2\text{CO}_3$ to form CaCO_3 which is precipitated; $\text{NaOH} + \text{CaCO}_3 \cdot \text{H}_2\text{CO}_3 = \text{HNaCO}_3 + \text{CaCO}_3 + \text{H}_2\text{O}$.

There is probably a reaction with CaCl_2 or CaSO_4 as NaOH will prevent scaling when these substances are present. It may be as follows:



The Ca(OH)_2 formed is soluble and would react with any Calcium or Magnesium bicarbonate present.

With $\text{MgCO}_3 \cdot \text{H}_2\text{CO}_3$, Mg(OH)_2 is formed, $\text{MgCO}_3 \cdot \text{H}_2\text{CO}_3 + 2\text{NaOH} = \text{Mg(OH)}_2 + 2\text{HNaCO}_3$. It removes Magnesium also if present in the form of chloride or sulphate.



But the feature which makes NaOH a particularly desirable reagent is the fact that it removes sulphates and carbonates at

the same time. Thus if $\text{CaCO}_3 \cdot \text{H}_2\text{CO}_3$ and MgSO_4 were both present in a water, CaCO_3 and $\text{Mg}(\text{OH})_2$ would be precipitated on the addition of NaOH and HNaCO_3 ^{would} remain in solution as shown above.

Barium hydrate is an ideal reagent for softening water. Both the carbonate and sulfate are insoluble, so no salts remain in solution as is the case when soda ash or sodium hydrate is used. Barium hydrate reacts with $\text{CaCO}_3 \cdot \text{H}_2\text{CO}_3$ to form BaCO_3 and CaCO_3 both of which are insoluble.



With CaSO_4 it forms insoluble BaSO_4 and $\text{Ca}(\text{OH})_2$ which would react with any $\text{MgCO}_3 \cdot \text{H}_2\text{CO}_3$, forming $\text{Mg}(\text{OH})_2$ and CaCO_3 , all of which are insoluble. With CaCl_2 no ^{precipitation} reaction would take place.

If the water contained $\text{MgCO}_3 \cdot \text{H}_2\text{CO}_3$ insoluble BaCO_3 and $\text{Mg}(\text{OH})_2$ would result. ~~No action with the chloride of Magnesium.~~

Conclusion; Barium hydrate is an exceptionally good reagent because it leaves no salts in solution after reacting with any sulfates, ~~chlorides~~ or carbonates in the water. Barium is not used commercially to any extent on account of its high price due to a scarcity of its compounds in nature and the difficulty of obtaining the carbonate or hydrate from the sulfate, (BaSO_4), which is the form that occurs in largest quantity in nature.

There is a considerable number of other reagents that are used at times in water treatment. They are not so generally applicable as those mentioned above or are too expensive for ordinary use but may be useful in special cases. Among these

may be mentioned silicate of soda, Na_2SiO_3 , oxalate of soda, $\text{Na}_2\text{C}_2\text{O}_4$, tri-sodium phosphate, Na_3PO_4 , Sugar, and tannic extract.

In this connection the action of heat on waters containing bicarbonates must not be overlooked. When such a water is heated, the CO_2 in solution is driven off and the normal carbonates of Calcium and Magnesium are deposited thus removing a certain amount of the total hardness. The hardness thus removed is known as the temporary hardness. Waters are very frequently heated to remove the temporary hardness before treatment, leaving the permanent hardness to be dealt with by the reagent used, ~~lime or soda~~.

In certain cases a water may not require treatment for removing incrusting and scale forming constituents but may have so much turbidity that a clarification is needed. In such cases alum, or ferrous sulfate, and lime or soda are often employed. The process consists in the formation of a gelatinous precipitate of Iron or Aluminium hydrate which on settling out carries down with it the suspended matter. The use of lime or soda ash in conjunction with the alum or iron sulfate is required only when the water does not contain enough carbonates to form sufficient aluminium or iron hydrate to effect the clarification. It must be noted that treatment of water in this manner does no other service than to remove suspended impurities. The permanent hardness is increased, since when lime is added with the alum or iron sulfate, CaSO_4 is formed and remains in solution. Sulphates are also formed by reaction with the acid carbonates

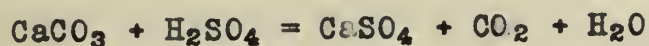
A slight description of the methods of analysis and the terms used in expressing the results in this thesis will not be out of place. All of the determinations made come under the head of Mineral Analyses and of these only the methods for the determination of Alkalinity, Calcium, Magnesium, hardness and incrustants need be considered.

Hehner devised the method used at present for determining the alkalinity or temporary hardness. He used N/10 HCl and methyl orange as indicator. Other methods are merely modifications of Hehners method, in using different strengths of acid employed and in the use of different indicators. Among the indicators proposed, may be mentioned phenacetolin lacmoid, erythrosine and alizarine. The use of lacmoid or erythrosine in determining alkalinity is recommended by the Committee on Standard Methods of Water Analysis.*

*Journal Infectious Diseases, Supplement No.1, May 1905.

The following procedure has been carried out in this work.

100 c.c. of sample are placed in a 200 c.c. flask and three drops of methyl orange added. A white tile or paper is placed underneath to show the color more readily and it is titrated with N/50 H₂SO₄. The number of c.c. used, multiplied by ten, gives the temporary hardness in parts per Million in terms of CaCO₃.



Methyl orange gives the total temporary hardness, plus the alkalinity due to alkali salts that is, the alkalinity to carbonates, bicarbonates and any hydrate ions which may be present.

Phenolphthalein reacts acid to bicarbonates and not to the normal carbonates. When a water containing normal carbonates is titrated with phenolphthalein as an indicator only one half the normal carbonate is indicated because the acid sets free an equal amount of CO_2 which has an acid reaction for this indicator. Thus when the phenolphthalein alkalinity is just one half of the methyl orange alkalinity it shows that all of the alkalinity is caused by normal carbonates.

In our work the phenolphthalein alkalinity was determined in the same sample and previous to the methyl orange determination of the alkalinity.

The Calcium may be determined by both gravimetric and volumetric methods. In the gravimetric method the Calcium is precipitated as the oxalate and ignited forming the oxide, CaO , in which form it is weighed. This is the most accurate method for Calcium, but requires considerable manipulation and time. The volumetric method consists in precipitating the Calcium as the oxalate, dissolving in dilute H_2SO_4 and titrating with standard KMnO_4 .

This method is rapid and if carefully and consistently carried out seems to give reliable results.

We used this method in our work, following an outline devised by Hale for the determination of Calcium in waters.*

*Hale F. E. J. A. C. S. Aug. 1907.

Following is the procedure: To 100 c.c. of sample add 10 c.c. of a saturated solution NH_4Cl and 1 c.c. 1 : 1 NH_4OH . Add 5 c.c. of a saturated solution oxalic acid and 5 c.c. of a saturated solution $(\text{NH}_4)_2\text{C}_2\text{O}_4$. Boil vigorously fifteen minutes, filter and wash with hot water. Dissolve the precipitate on the filter with a few c.c. of hot dilute H_2SO_4 and titrate hot with KMnO_4 , subtracting .3 c.c. for blank. The KMnO_4 is of such strength that 1 c.c. equals 10 parts per Million of Calcium as CaCO_3 .

Of the methods for the determination of Magnesium, besides the standard gravimetric method in which the Magnesium is precipitated as ammonium, Magnesium phosphate and then changed by ignition into the pyrophosphate, several^{al} short methods have been proposed which deserve some attention.

In one of these methods a certain volume of lime water is added to 100 c.c. of the sample to be analyzed, after carefully neutralizing to methyl orange and boiling to expel CO_2 . It is then heated on water bath, then allowed to cool and made up to a standard volume. An aliquot portion of the filtrate is titrated with $\text{N}/50\text{H}_2\text{SO}_4$ and methyl orange. A blank of distilled water is run at the same time. The difference between the amount of acid required for the blank and that for the sample represents the amount of Magnesium present, in terms of CaCO_3^* .

*Pfeifer & Wartha, Zeit. Fur Ang. chemie 1902 (198)

Among the objections to the method is the fact that lime water attacks ordinary glass vessels quite strongly when boiled in them. If hard Jena glass flasks are used the action is very small. Then, too, experiment has shown that filter papers may in some cases react either acid or alkaline.*

* J. S. C. I. Proctor 23-8.

But since a blank is run at the same time such errors would occur in it also and thus be eliminated. Mr. J. M. Lindgren preliminary study for his used this method in his thesis work and seemed to get very satisfactory results with it.*

*J. M. Lindgren, Thesis for Master's Degree, U. of I. 1907, p 24.

Reaction involved is $\text{MgSO}_4 + \text{Ca(OH)}_2 = \text{Mg(OH)}_2 + \text{CaSO}_4$.

One method quite frequently used is titration of a nitric acid solution of MgNH_4PO_4 by Uranium nitrate. This method is recommended by some analysts and was tried in our work. Following was a method of procedure, as outlined by the U. S. G. S. To the cold filtrate from the Calcium determination, 5 c.c. of a saturated solution of $\text{Na}_2\text{NH}_4\text{PO}_4$ was added, stirred thoroughly, 3 c.c. ammonia added and allowed to stand over night. The solution was filtered and the precipitate washed with dilute ammonia then dissolved on the filter by

washing with dilute HNO_3 . 1-10, collecting the washings in the original beaker. One drop of methyl orange was added and then strong ammonia was run in until the solution was alkaline. It was then titrated back with dilute HNO_3 until just barely acid 5 c.c. of Sodium acetate solution was then added and the liquid heated to boiling. It was then titrated hot with the standard Uranium nitrate solution using potassium ferrocyanide as outside indicator.

We first used this method for determining the Magnesium in a series of samples obtained in treating the University water with Na_3PO_4 . The results obtained were quite irregular and did not seem to be correct. In order to test the method a series of solutions of MgSO_4 were made up containing from 20, to 200 parts per Million of MgSO_4 as CaCO_3 . These solutions were then analysed for Magnesium. The results did not accord with the theory, this being true especially with the solutions which contained the least amounts of Magnesium. The following table shows the amounts of Magnesium present and found.

1. The first part of the paper is devoted to a general
discussion of the problem. It is shown that the
problem is of great importance in the theory of
the differential equations of the second order.
The second part of the paper is devoted to a
detailed study of the problem. It is shown that
the problem is of great importance in the theory
of the differential equations of the second order.
The third part of the paper is devoted to a
detailed study of the problem. It is shown that
the problem is of great importance in the theory
of the differential equations of the second order.
The fourth part of the paper is devoted to a
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the problem is of great importance in the theory
of the differential equations of the second order.
The fifth part of the paper is devoted to a
detailed study of the problem. It is shown that
the problem is of great importance in the theory
of the differential equations of the second order.

As parts per Million of CaCO_3

No.	Mg. Present.	Mg. Found.
1.	20	79
2.	40	140
3.	60	167
4.	80	144
5.	100	125
6.	120	155
7.	140	167
8.	160	186
9.	180	197
10.	200	209

The solution used was of such strength that 1 c.c. = .0038 g. Magnesium as CaCO_3 . There was much difficulty in determining the exact end point. A brownish coloration appeared some time before the true end point was reached and made it very hard to tell just when the true end point was reached. As a means of lessening these errors, a portion of the Uranium solution was diluted up until 1 c.c. = .001 g. Magnesium as CaCO_3 and the first five of the previous standard solutions analyzed again. The results were as follows:

THE HISTORY OF THE

1790	1791	1792	1793	1794	1795	1796	1797	1798	1799
1790	1791	1792	1793	1794	1795	1796	1797	1798	1799
1790	1791	1792	1793	1794	1795	1796	1797	1798	1799
1790	1791	1792	1793	1794	1795	1796	1797	1798	1799
1790	1791	1792	1793	1794	1795	1796	1797	1798	1799
1790	1791	1792	1793	1794	1795	1796	1797	1798	1799
1790	1791	1792	1793	1794	1795	1796	1797	1798	1799
1790	1791	1792	1793	1794	1795	1796	1797	1798	1799
1790	1791	1792	1793	1794	1795	1796	1797	1798	1799
1790	1791	1792	1793	1794	1795	1796	1797	1798	1799

The first part of the history of the United States is the history of the colonies. The colonies were founded by Englishmen, and they were governed by English laws. The colonies were at first dependent on England, but they gradually became more independent. The colonies were at first small, but they grew larger and larger. The colonies were at first poor, but they became richer and richer. The colonies were at first weak, but they became stronger and stronger. The colonies were at first divided, but they became united and united.

THE HISTORY OF THE UNITED STATES

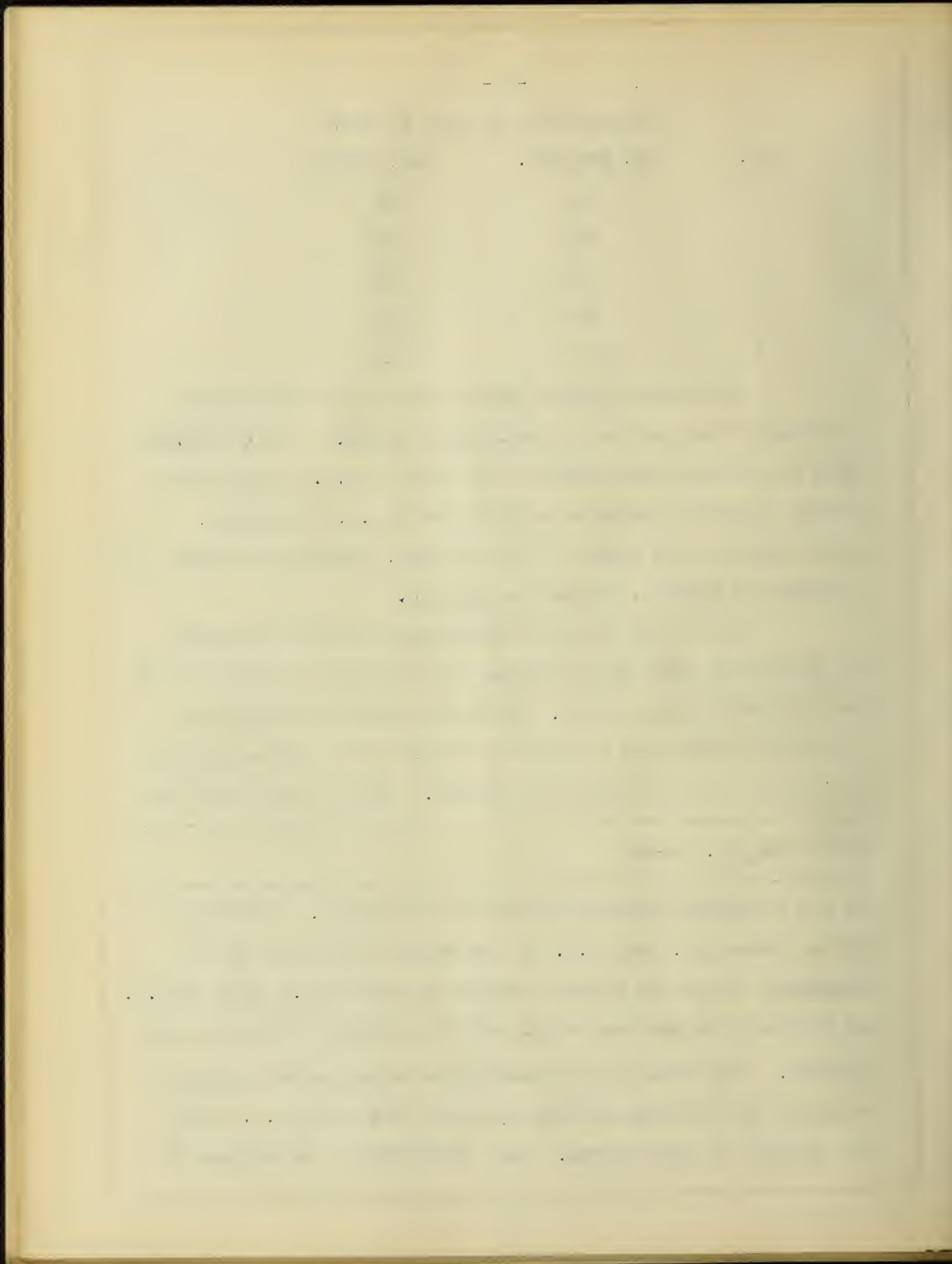
As parts per Million of CaCO_3		
No.	Mg. Present.	Mg. Found.
1	20	51
2	40	58
3	60	80
4	80	102
5	100	119

The method finally decided upon for use in these experiments was the usual gravimetric method. To the filtrate from the Calcium determination was added 5 c.c. of saturated sodium ammonium phosphate solution and 3 c.c. of ammonia. After standing all night it was filtered, washed with dilute Ammonia and ignited. Weighed as $\text{Mg}_2\text{P}_2\text{O}_7$.

It is very often of assistance to know the amount of incrusting salts, the chlorides and sulfates of Magnesium and Calcium, present in a water. There are several methods for determining these but the best in point of ease and accuracy is the one devised by Pfeiffer and Wartha.* Their method was used

*Zeit fur Ang. Chemie

in all incrustant determinations in this thesis. Following is the procedure. 200 c.c. of the sample are boiled in an Erlenmeyer flask for fifteen minutes to expel CO_2 . Then 25 c.c. of N/10 soda reagent are added and the solution boiled for ten minutes. (The soda reagent consists of equal parts of Na_2CO_3 + NaOH) The solution is then filtered into a 200 c.c. flask and diluted to that volume. The alkalinity is determined in



an aliquot portion using N/50 H_2SO_4 and methyl orange. A blank determination is run at the same time using distilled water. The difference between the sample and the blank is the incrustants in terms of CaCO_3 . If the blank determination is less than that of the water, it shows that the water contains Na_2CO_3 .

In a few cases the total hardness was determined by the soap method. The procedure was that generally prescribed in text books, with one slight modification. With waters containing much Magnesium, the end point is difficult to determine accurately. To eliminate this error Mr. C. Arthur Brown of the Am. Steel & Wire Co., suggested that the water be neutralized to methyl orange with H_2SO_4 before using the soap method. This was done in all cases and aided in determining the end point, more accurately.

The general plan followed in the experimental part of this thesis was to select three or four waters of different types, that is, water varying as widely as possible in the amount and character of the impurities contained in them, and to treat them in turn with different softening reagents. In detail the method was as follows; One liter of the water under investigation was placed in each of nineteen large, glass stoppered, bottles, and, leaving the first one untreated, increasing amounts of the reagent were added to the remaining samples. The reagent was made up of a definite strength; after standing over night the samples were filtered into another set of glass stoppered bottles. The alkalinity, Calcium and

Magnesium were then determined for each sample.

The first water treated was the University water. This is a type of water containing bicarbonates of the alkalies and alkaline earths. The analysis of this water made by standard methods gave the following results:

University of Illinois Water.

HYPOTHETICAL COMBINATIONS.

Parts per Million.

Potassium chloride	KCl	2.9
Sodium chloride	NaCl	3.5
Sodium sulphate	Na ₂ SO ₄	3.6
Magnesium carbonate	MgCO ₃	121.2
Calcium carbonate	CaCO ₃	175.2
Sodium carbonate	Na ₂ CO ₃	60.5

Nineteen samples of one litre each were measured into glass stoppered bottles and treated with varying amounts of Na₃PO₄ solution. The next day they were filtered and the alkalinity and Calcium and Magnesium content determined as above described. The following table shows the amounts of Na₃ PO₄ in terms of CaCO₃ and the results of the determinations.

TABLE I.

TREATMENT OF UNIVERSITY WATER WITH Na_3PO_4 .

No.	Na_3PO_4 c.c. Sol.	Na_3PO_4 as CaCO_3	Alkal. to Ph'thalein	Alkal. to M. Orange	KMnO_4 required	CaCO_3	$\text{Mg}_2\text{P}_2\text{O}_7$ from 100 c.c.	Mg as CaCO_3
		Milli- grams	Parts per Million	Parts per Million		P'ts per Milli- Million	grams	P'ts per Million
1	0	0	0	386.	18.3	183.	.0173	179.
2	1	5.8	0	398.	18.3	183.	.0171	179.
3	2	11.6	0	413.	17.4	174.	.0172	179.
4	4	23.2	0	423.	13.9	139.	.0164	170.
5	6	34.8	0	426.	10.9	109.	.0161	167.
6	7	40.6	.9	435.	9.8	98.	.0150	156.
7	8	46.4	1.2	437.	7.8	78.	.0149	144.
8	10	58.0	1.4	444.	5.2	52.	.0125	130.
9	12	69.6	1.5	468.	4.0	40.	.0125	130.
10	14	81.2	1.8	483.	2.8	28.	.0108	112.
11	16	92.8	2.3	522.	2.8	28.	.0101	105.
12	17	98.6	2.0	542.	2.4	24.	.0101	105.
13	18	104.4	2.2	557.	3.4*	16.0	.0203*	105.
14	20	116.0	2.5	585.	2.7	13.5	.0169	87.
15	22	127.6	5.5	607.	2.2	11.0	.0151	78.
16	24	139.2	6.0	655.	2.3	11.5	.0150	78.
17	26	150.8	7.4	676.	2.0	10.0	.0120	62.
18	28	162.4	9.0	707.	1.3	6.5	.0136	70. (?)
19	30	174.0	15.1	816.	.7	3.5	.0100	52.

*200 c.c. sample.

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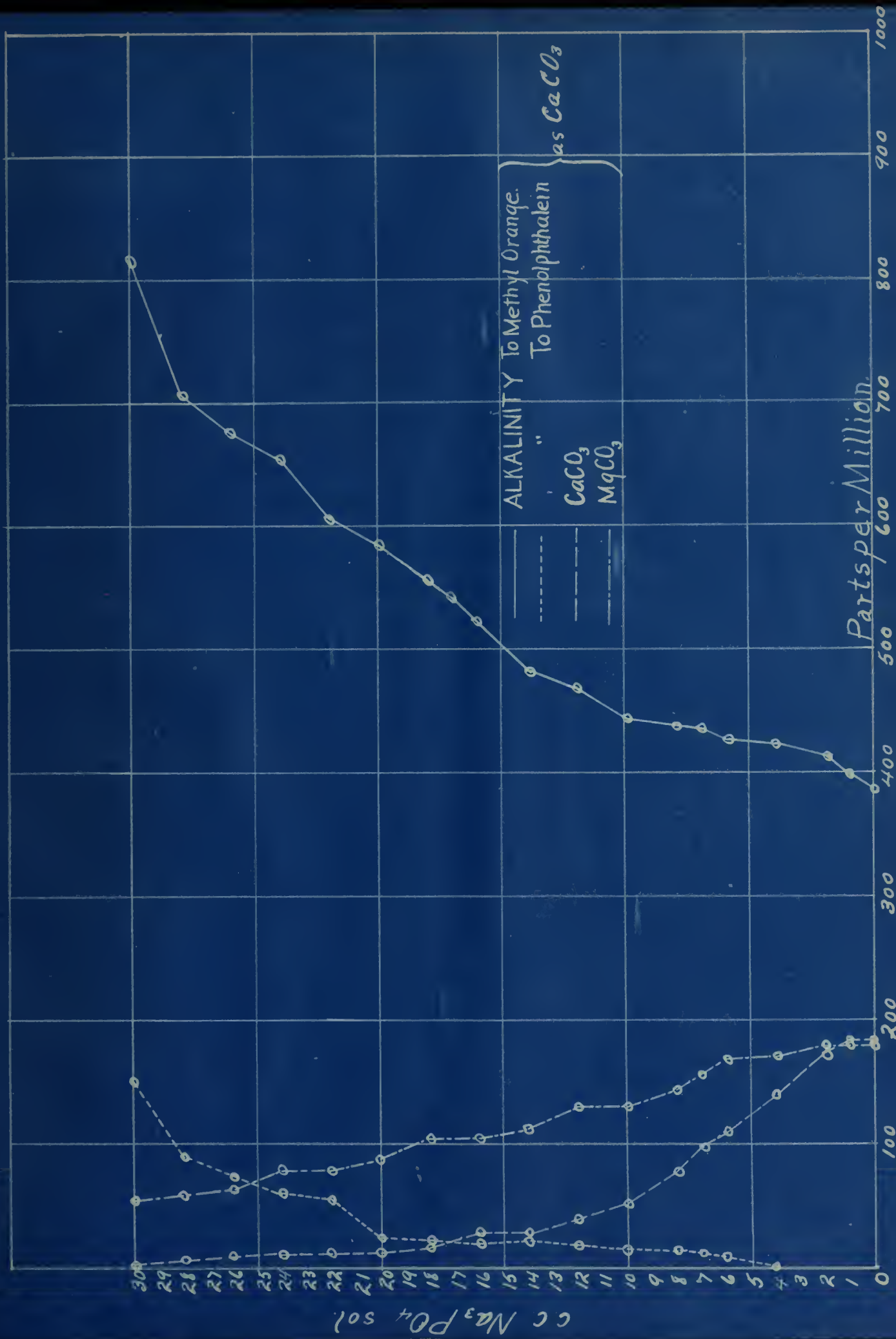
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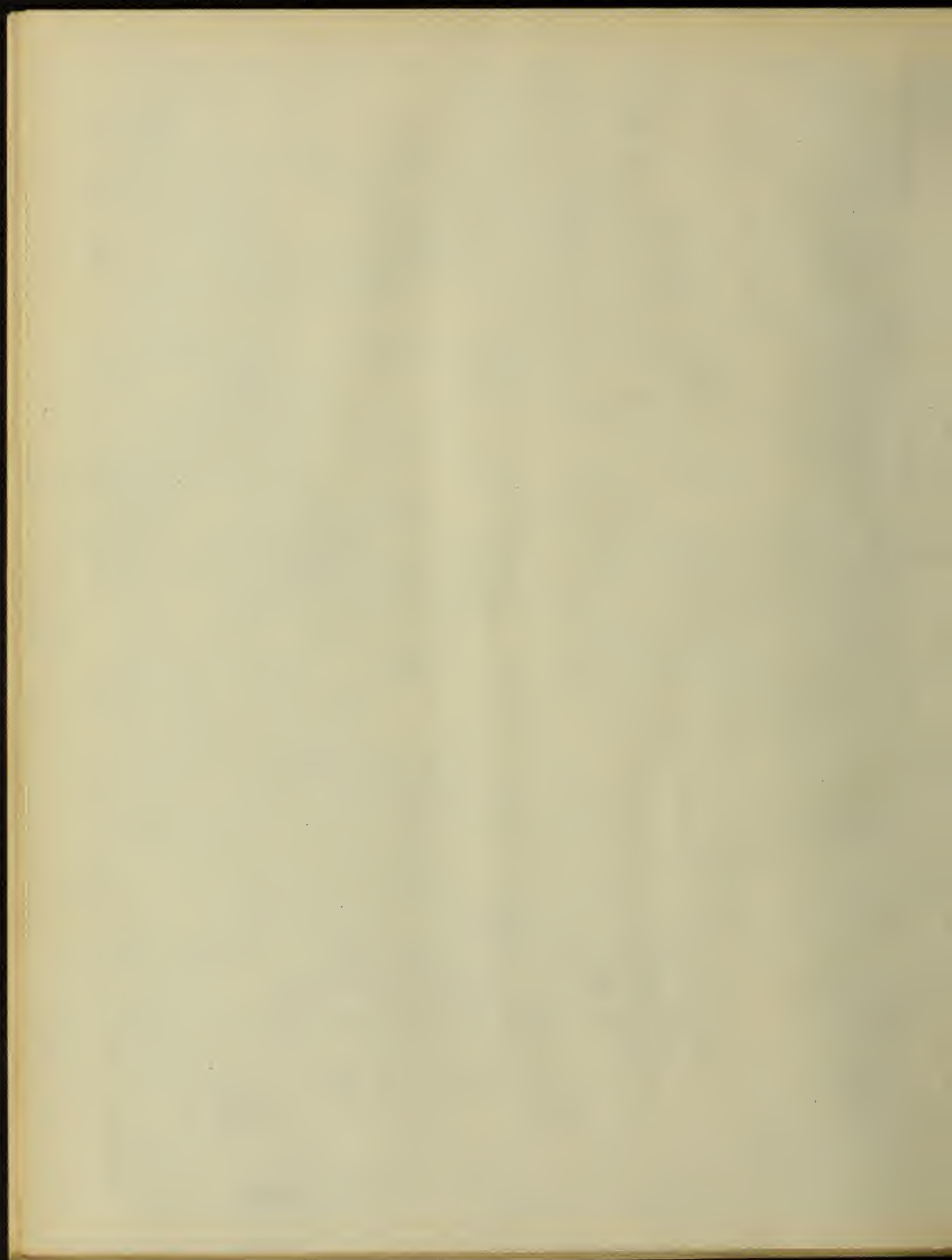
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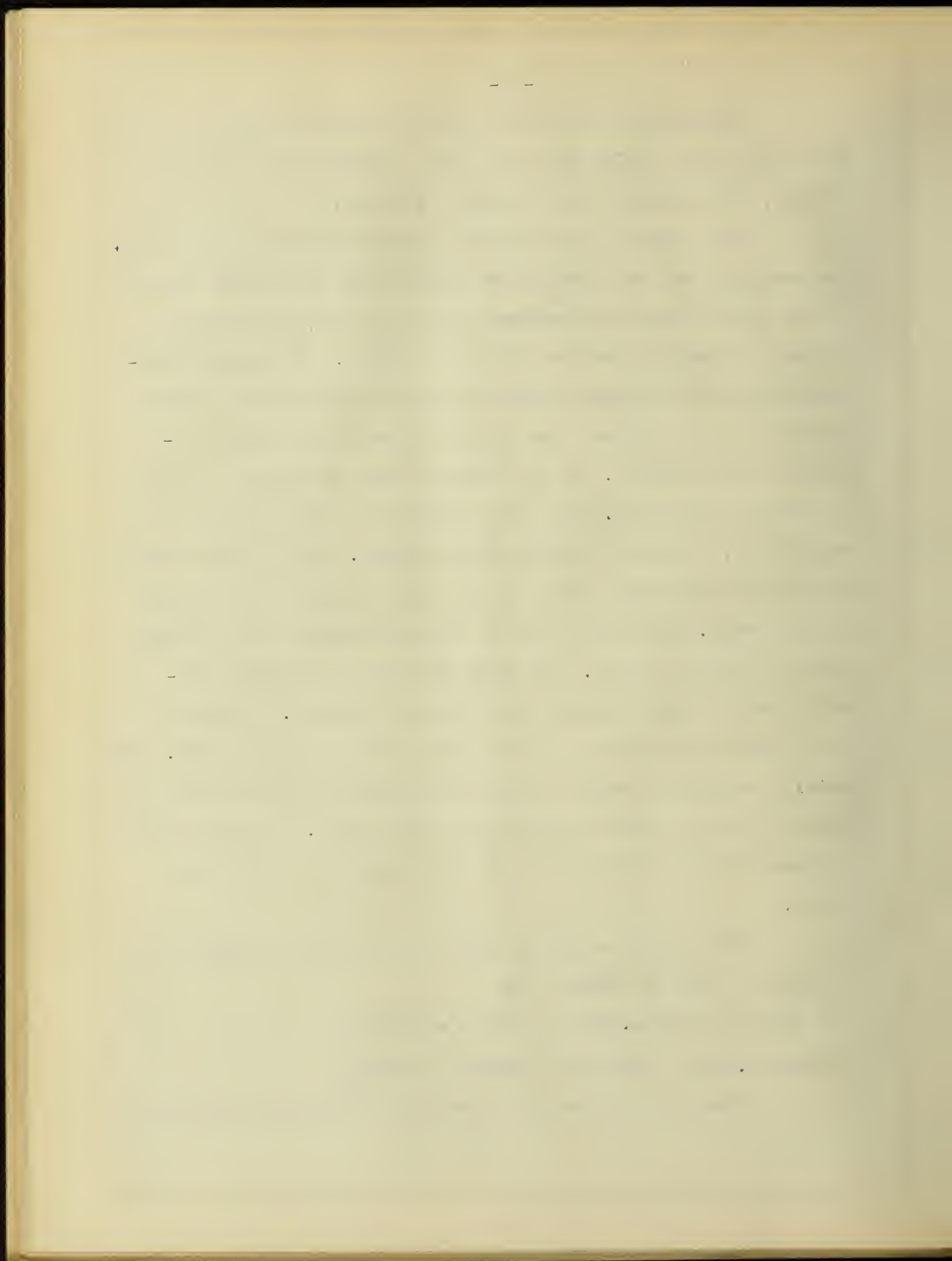
Before discussing the results it may be well to note that Na_3PO_4 is broken up in water solution into $\text{NaOH} + \text{HNa}_2\text{PO}_4$, thus; $\text{Na}_3\text{PO}_4 + \text{H}_2\text{O} = \text{NaOH} + \text{HNa}_2\text{PO}_4$.

The results are expressed diagrammatically in Plate I. The reactions may be regarded as taking place in several stages. In the first stage the reaction seems to be between the free CO_2 and the NaOH (formed as described above). The phenolphthalein alkalinity remains negative and the Magnesium and Calcium content does not change; the alkalinity to methyl orange increases quite rapidly. In the second stage the HNa_2PO_4 begins to react on the $\text{CaCO}_3 \cdot \text{H}_2\text{CO}_3$ and results in a rapid decrease in the content, insoluble CaHPO_4 being formed. The Calcium falls rapidly and the methyl orange alkalinity increases at a fairly constant rate. The alkalinity to phenolphthalein has a slight gradual increase from 0. The Magnesium goes out fairly uniformly but at a much slower rate than the Calcium. In the third stage the Calcium is still going out, and is very low. The phenolphthalein and methyl orange are increasing very rapidly showing that an excess of Na_3PO_4 has been added. The Magnesium continues to come out at about the same rate as in the other stages.

The reactions taking place in the various stages are:

- (1) $\text{NaOH} + \text{H}_2\text{CO}_3 = \text{HNaCO}_3 + \text{H}_2\text{O}$
- (2) $\text{HNa}_2\text{PO}_4 + \text{CaCO}_3 \cdot \text{H}_2\text{CO}_3 = \text{CaHPO}_4 + 2\text{HNaCO}_3$
- (3) $\text{MgCO}_3 \cdot \text{H}_2\text{CO}_3 + \text{HNa}_2\text{PO}_4 = \text{HMgPO}_4 + 2\text{HNaCO}_3$

Thus it is clear that treatment with Na_3PO_4 is useless



in a water of this type so far as Magnesium is concerned. The Magnesium comes out only slowly even when large amounts of the reagent have been added. It removes Calcium very well but increases the alkalinity quite rapidly. The total solids would also increase, since in removing Calcium and Magnesium it leaves more than an equal weight of sodium salts (bicarbonate) in solution.

The treatment with Na_3PO_4 was then tried on the Kankakee River water. This water contains sulfate of Magnesium. Following is the average of the results of analyses for one year, made in the laboratory of the State Water Survey.

Kankakee River water.

HYPOTHETICAL COMBINATIONS.

		Parts per Million.
Sodium nitrate	NaNO_3	4.7
Sodium chloride	NaCl	6.3
Sodium sulphate	Na_2SO_4	19.1
Magnesium sulphate	MgSO_4	42.7
Magnesium carbonate	MgCO_3	29.8
Calcium carbonate	CaCO_3	119.8
Iron carbonate	FeCO_3	.5

The experiment was carried out in exactly the same way as in the previous case with the exception that only 12 samples were treated. The following table shows amounts of reagent and results of analysis.

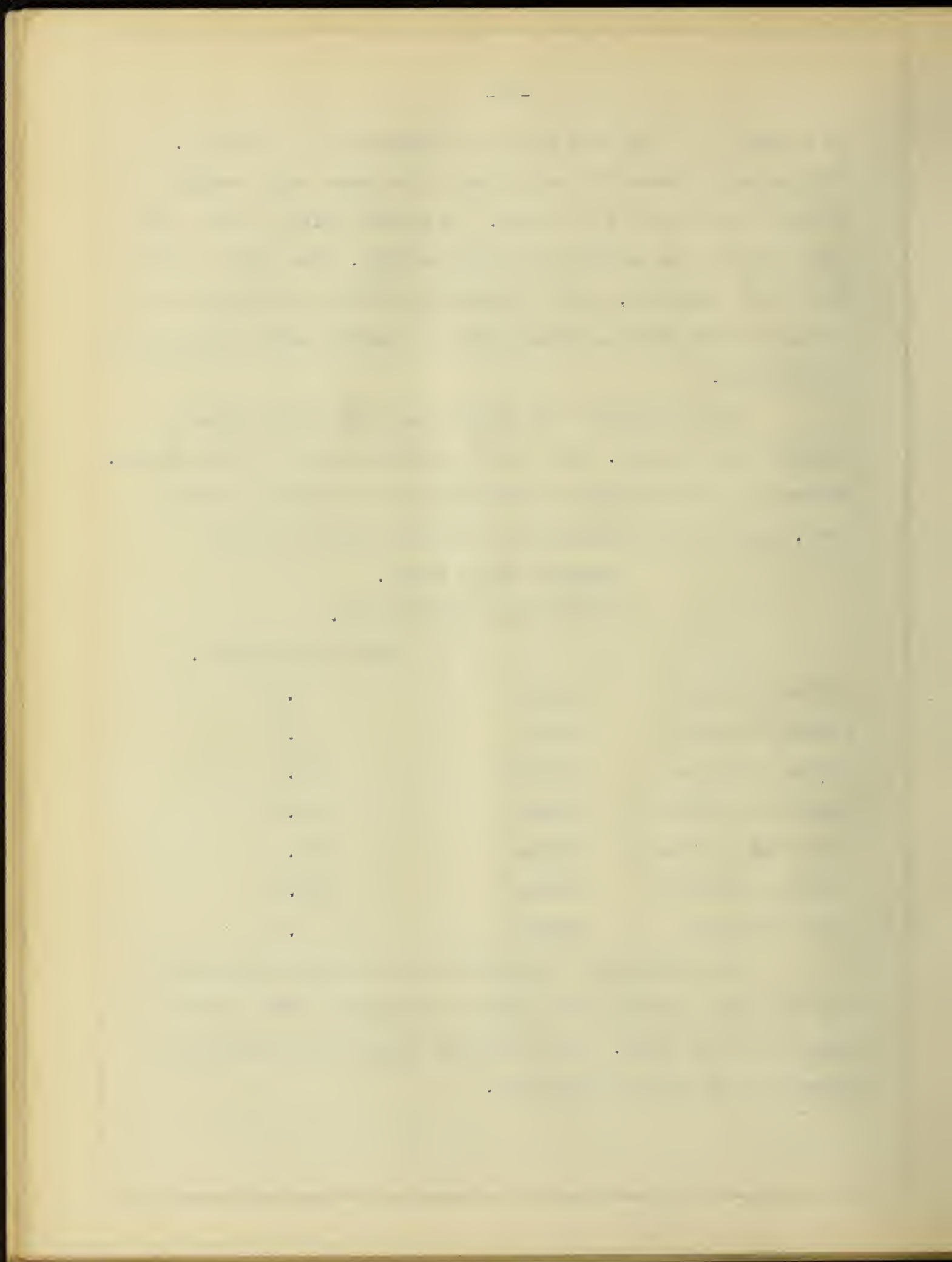


TABLE II.

TREATMENT OF KANKAKEE RIVER WATER WITH NaPO_4 .

No.	Na_3PO_4 c.c. Sol.	Na_2PO_4 as CaCO_3	Alkal. to Ph'thalein	Alkal. to M. Orange	KMnO_4 required	CaCO_3	$\text{Mg}_2\text{P}_2\text{O}_7$ from 100 c.c.	P'ts per Milli- grams	P'ts per Million
1	0	0	0	133	17.1	171	.0111	115	
2	1	5.8	3.	152	16.2	162.	.0105	109	
3	2	11.6	3.	155	15.2	152.	.0094	97	
4	4	23.2	4.	160	11.0	110.	.0087	90	
5	6	34.8	8.	161	7.6	76.	.0077	80	
6	7	40.6	10.	171	5.2	52.	.0072	74	
7	8	46.4	13.	176	4.3	43.	.0073	74	
8	9	52.2	16.	186	3.9	39.	.0069	71	
9	10.	58.0	24.	196	3.2	32.	.0057	59	
10	12.	69.6	38.	227	2.9	29.	.0047	48	
11	14.	81.2	51.	255	2.6	26.	.0032	33	
12	16.	92.8	70.	297	2.2	22.	.0024	25	

1 2 3 4 5 6 7 8 9 10

11 12 13 14 15 16 17 18 19 20

21 22 23 24 25 26 27 28 29 30

31 32 33 34 35 36 37 38 39 40

41 42 43 44 45 46 47 48 49 50

51 52 53 54

c.c. Na_3PO_4 sol.

30
29
28
27
26
25
24
23
22
21
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0

Parts per Million

300

400

500

600

700

800

900

1000

ALKALINITY To Methyl Orange
" To Phenolphthalein
as CaCO_3

— CaCO_3
- - - MgCO_3

Instants

0

100

200

300

400

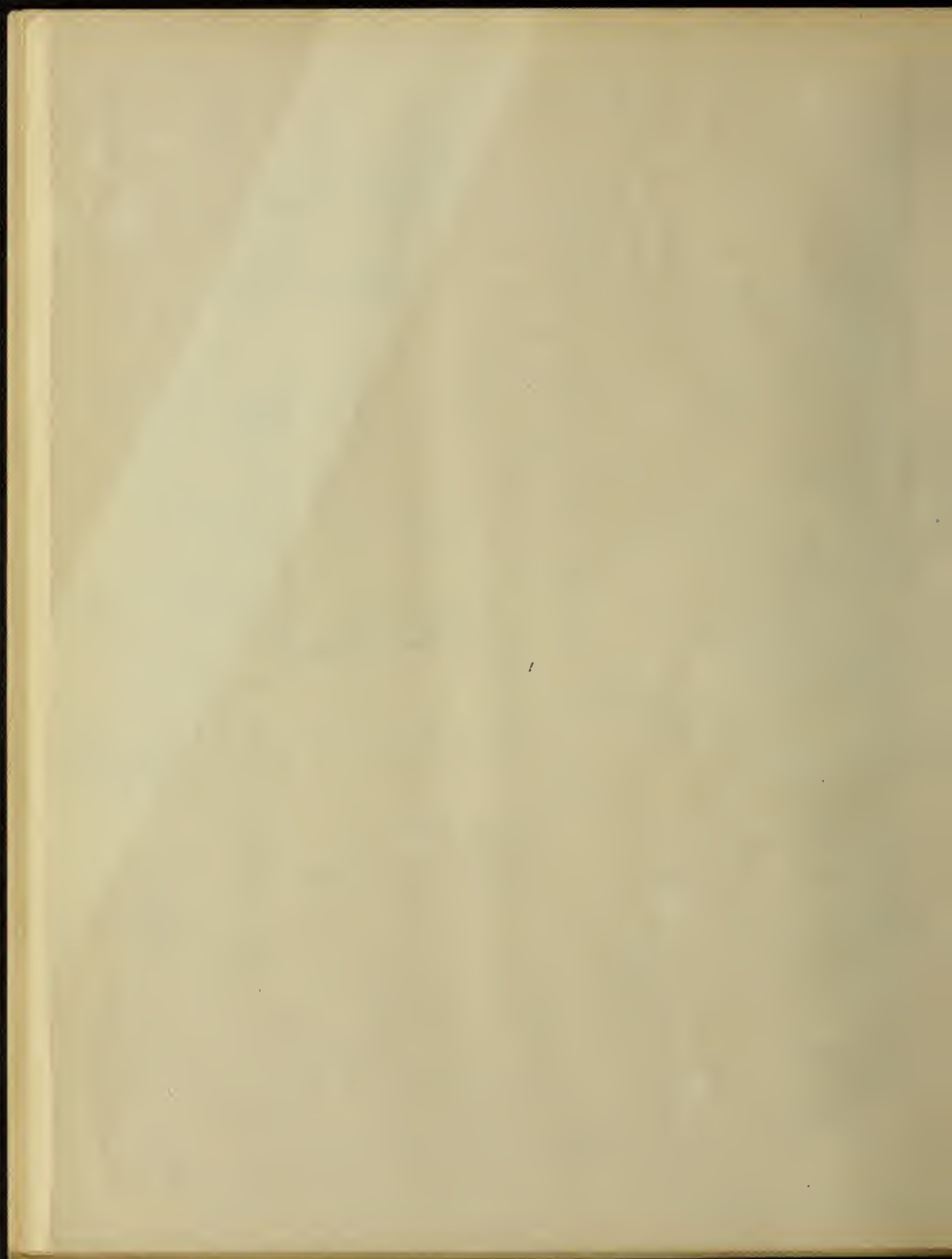
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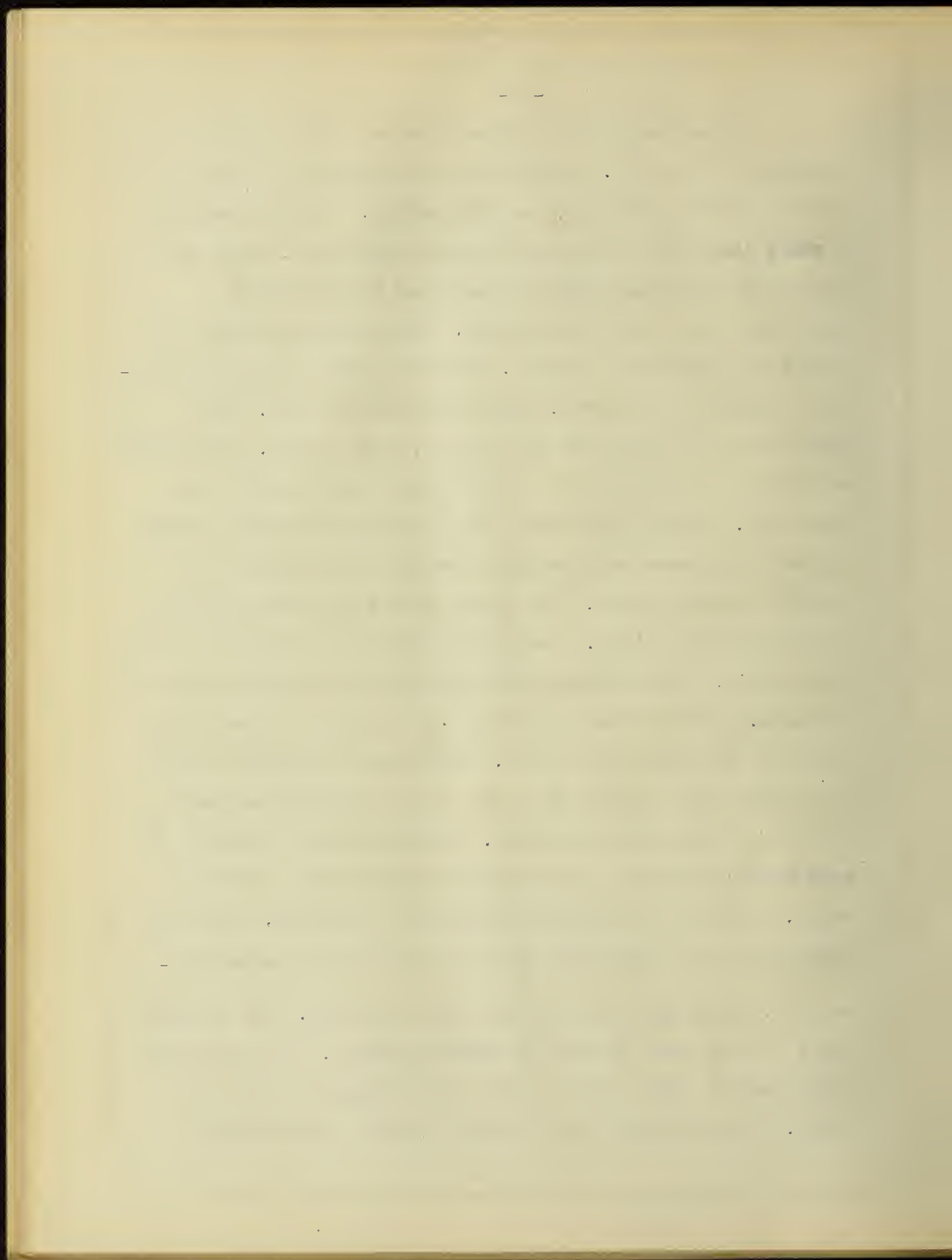
700

800

900



The diagrammatic representation of the analyses is given in Plate II. In this case the different stages of the reaction are harder to distinguish. We first notice a sharp increase in the methyl orange alkalinity, while the alkalinity to phenolphthalein increases throughout the experiment at a very uniform rate. The Calcium and Magnesium both come out nearly together. Then the methyl orange alkalinity increases very slowly, much slower than before. The Magnesium also comes down more slowly, than before. The Calcium continues to come out quite rapidly, much more so than the Magnesium. In the last stage the alkalinity to methyl orange begins to increase more rapidly showing that an excess of reagent has been added. The phenolphthalein alkalinity also increases more rapidly. The Calcium comes out much more slowly than before, while the Magnesium maintains its constant rate of decrease. The reactions involved are the same as those given above for the University water. Treatment with Na_3PO_4 seems to be much more efficacious in the case of this water than in that of the University water. The Magnesium is removed much more completely in this water than with the University water. This may be due to the absence of free CO_2 , since the phenolphthalein alkalinity shows the presence of normal carbonates, indicating that no free CO_2 is present. The Calcium curve is very much the same in the two waters. An incrustant determination shows only a small amount present in the raw water. This decreases very rapidly and the curve becomes



negative, showing the presence of an alkali.

The next water treated with Na_3PO_4 was from a shallow well at the plant of Dean and Bode Manufacturing Co., in Champaign. It contains bicarbonates and sulfates of the alkaline earths. An analysis made a few months previous showed the following results:

Water from Dean & Bode well.

HYPOTHETICAL COMBINATIONS.

		Parts per Million.
Sodium nitrate	NaNO_3	1.6
Sodium chloride	NaCl	39.6
Sodium sulphate	Na_2SO_4	53.7
Magnesium sulphate	MgSO_4	145.7
Magnesium carbonate	MgCO_3	36.4
Calcium carbonate	CaCO_3	263.0

This water was treated precisely like the preceding waters using the same strength of reagent. The following table and Plate III show the analytical data and their diagrammatic representation.

Referring to Plate III it is seen that at first the reaction is between the NaOH and free CO_2 just as in case of the University water. The methyl orange alkalinity rapidly increases at first then increases at a much slower rate. Both the Calcium and Magnesium are slowly decreasing. A second stage is noticeable when the methyl orange alkalinity increases only very slowly, as mentioned above, and the Calcium rapidly

TABLE III.

DEAN & BODE WELL WATER WITH Na_3PO_4 .

No.	Na_3PO_4 c.c. Sol.	Na_2PO_4 as CaCO_3	Alkal. to Ph'thalein	Alkal. to M. Orange	KMnO_4 required	CaCO_3	$\text{Mg}_2\text{P}_2\text{O}_7$ from 100 c.c.	Mg as CaCO_3
		Milli- grams	Parts per Million	Parts per Million		P'ts per Milli- Million	Grams	P'ts per Million
1	0	0	0	311.	21.5	215	.0193	200.
2	1	5.8	0	345.	20.0	200	.0199	206.(?)
3	2	11.6	0	353.	19.6	196	.0189	196.
4	4	232.	0	357.	15.	150	.0185	192.
5	6	34.8	6.	360.	11.7	117	.0174	181.
6	7	40.6	7.	366.	9.7	97	.0173	180.
7	8	46.4	9.	369.	7.3	73	.0161	167.
8	10	58.0	13.	377.	6.3	63	.0146	151.
9	12	69.6	20.	394.	4.5	45	.0135	140.
10	14	81.2	34.	416.	3.7	37	.0199	123.
11	16	92.8	40.	443.	3.2	32	.0089	92.
12	17	98.6	40.	451.	2.4	24	.0085	99.
13	18.	104.4	60.	471.	2.9*	14.5	.0161*	83.5
14	20.	116.0	75.	498.	2.7	13.5	.0150	77.
15	22	127.6	92.	527.	2.2	11.	.0134	69.
16	24	139.2	93.	559.	1.6	8.	.0128	66.
17	26	150.8	114.	593.	1.6	8.	.0114	59.
18	28	162.4	144.	626.	1.0	5.	.0112	58.
19	30.	174.	150.	655.	.9	4.5	.0101	52.

*200 c.c. sample.

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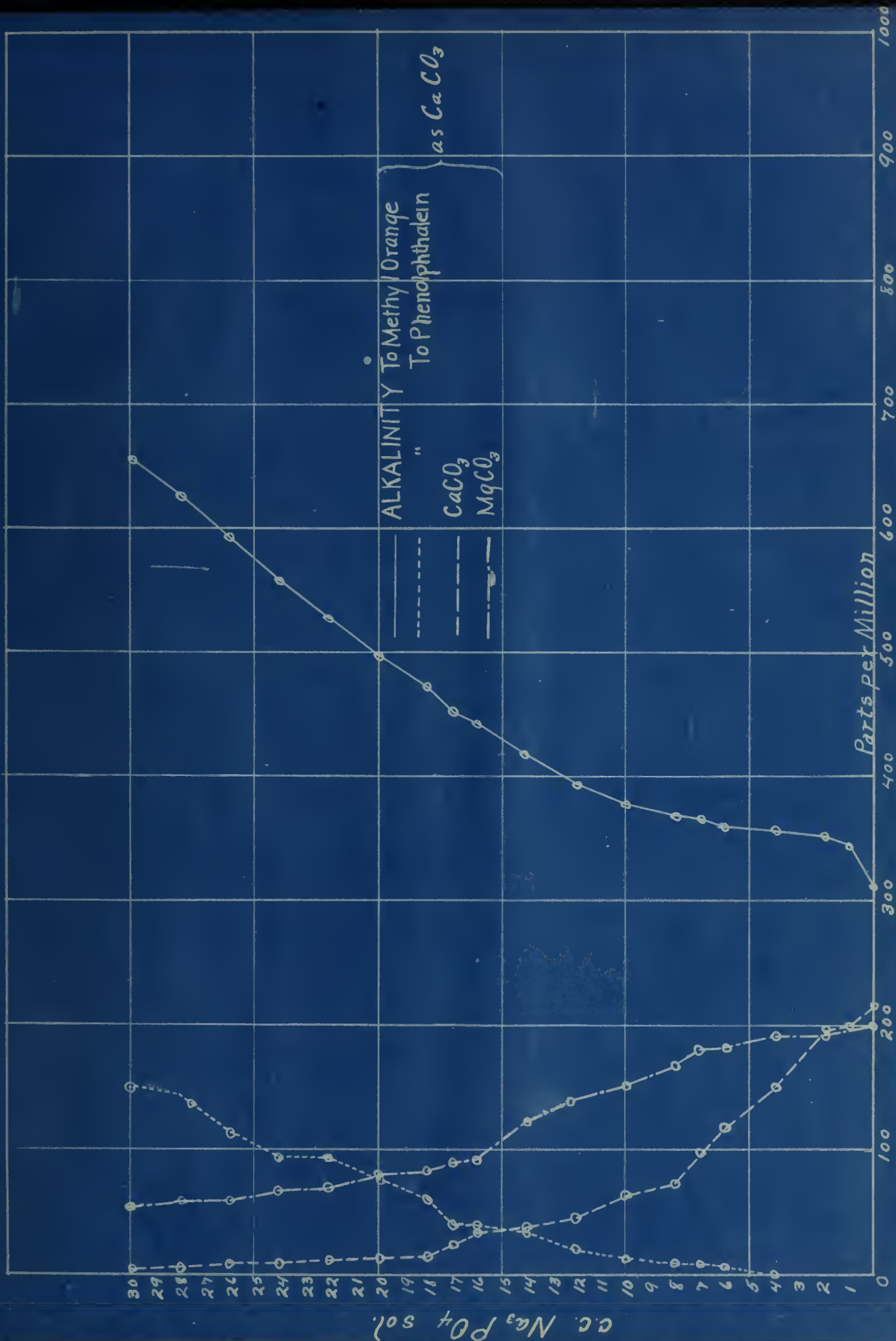
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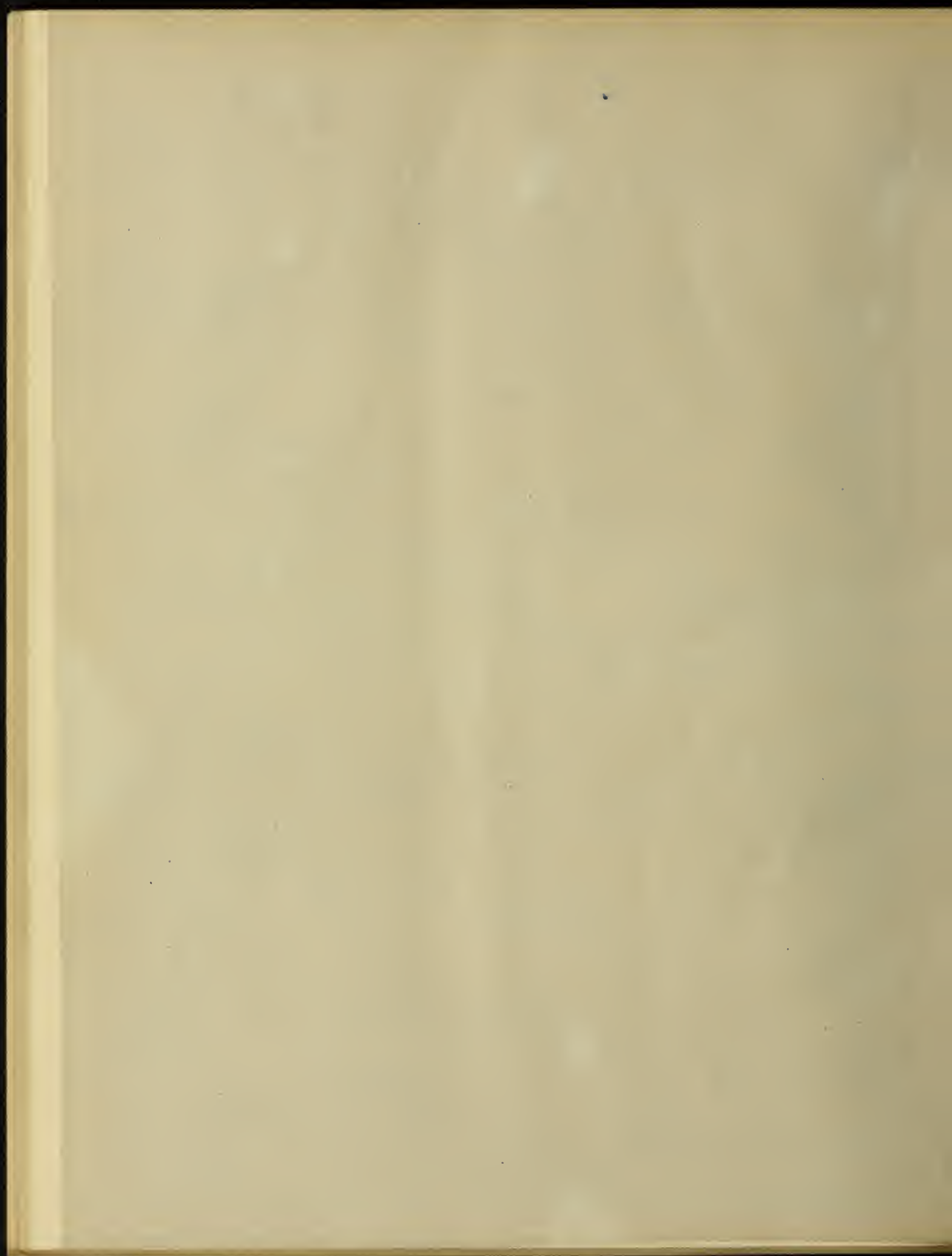
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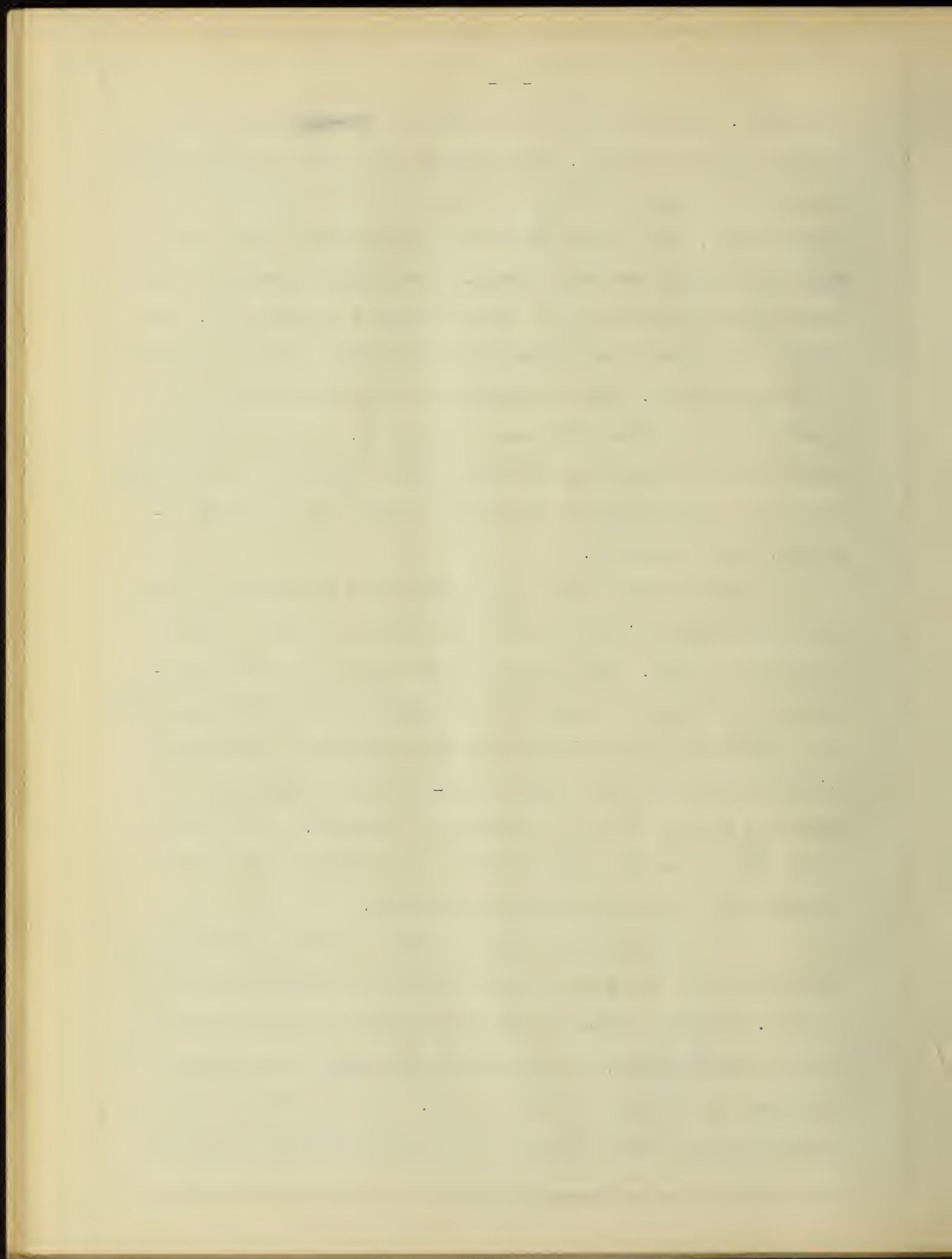


decreases. The Magnesium also comes out though much more slowly than the Calcium. During this stage the phenolphthalein alkalinity begins a gradual increase. A third stage may be noticed when, the rate of decrease of Calcium and Magnesium suffers a slight change in speed. The Calcium comes out more rapidly while the Magnesium is removed at a slower rate. The methyl orange and phenolphthalein curves show a similar change at the same place, both exhibiting a slight decrease in the speed with which they have been increasing. In the last stage the Calcium and Magnesium decrease quite uniformly side by side while the phenolphthalein and methyl orange alkalinities increase, quite steadily.

It is clear from the diagram that treatment of this water with Na_3PO_4 alone is not sufficient to remove all objectionable salts. The Calcium is removed only by the addition of considerable quantities of reagent, while the Magnesium is removed still more slowly and incompletely. As is seen it is possible to remove only three-fourths of the total Magnesium content even by an excess of reagent. As is seen the curves correspond quite closely with those obtained by treating the University water with Na_3PO_4 .

In conclusion; we may say that treatment with Na_3PO_4 does not appear to be highly successful in the cases just studied. Briefly summed up the objections to its use are:

- (1) It removes Magnesium imperfectly and only after large amounts of the reagent have been used.
- (2) The total solids increase rather than decrease.
- (3) The alkalinity increases



very markedly.

The next experiment was to treat a water containing sulfates and carbonates of the alkalies and alkaline earths. This water was obtained from one of the deep wells of the Mattoon Clear Water Co., of Mattoon, Illinois. An analysis sometime previous gave:

Mattoon City Water.

HYPOTHETICAL COMBINATIONS.

Parts per Million.		
Sodium chloride	NaCl	20.
Sodium sulphate	Na ₂ SO ₄	66.
Magnesium sulphate	MgSO ₄	.6
Magnesium carbonate	MgCO ₃	129.
Calcium carbonate	CaCO ₃	332.
Iron Carbonate	FeCO ₃	6.

The experiment was carried out as in the previous cases using a saturated solution of lime water. The following table gives the analytical data. Plate IV gives the diagrammatic representation of the results.

An examination of the diagram shows that the reaction takes place in several stages. On the first stage the Ca(OH)₂ reacts with free CO₂ increasing the alkalinity to methyl orange, the Calcium content slightly increases, while the Magnesium decreases slightly. In the second stage a reaction between the Calcium acid carbonate and the Ca(OH)₂ takes place, causing the Calcium to be thrown out rapidly. In this stage the Calcium content and methyl orange alkalinity decrease quite uniformly

The first thing I noticed when I stepped out of the car was the cold. It was a sharp contrast to the warm blanket I had been sitting under. I looked up at the sky, which was a pale, overcast grey. The air was still, and the silence was heavy. I took a deep breath, feeling the cold air fill my lungs. I knew this was the beginning of something new, and I was ready for whatever came next.

I walked towards the building, my footsteps echoing on the wet pavement. The rain had just stopped, leaving the ground glistening. I could see my reflection in the puddles, a small figure in a dark coat. I felt a sense of purpose, a drive to see this through to the end.

I entered the building, the door creaking behind me. The interior was dimly lit, with light streaming in from the windows. I saw a desk with a lamp, a chair, and a door at the end of the hallway. I walked towards the door, my heart pounding. I knew what was on the other side, and I was determined to face it. I opened the door, and the light hit me. I stood there for a moment, taking in the sight before me. It was exactly what I needed.

I turned back, looking at the door I had just opened. I felt a sense of closure, a finality. I knew this was the end of a long journey, and I was proud of what I had accomplished. I closed the door, and the silence returned. I walked back to the car, my mind at peace.

I got into the car, the engine humming. I looked out the window, watching the rain fall. I felt a sense of freedom, a release. I knew I was going to miss this place, but I was also excited for what was ahead. I started the car, and I drove away, leaving the past behind me.

I drove for hours, the road winding through the landscape. The sun was low in the sky, casting a golden glow over everything. I felt a sense of wonder, a awe. I knew this was a special moment, a moment that would stay with me for the rest of my life. I smiled, feeling the wind on my face.

I stopped at a gas station, the attendant looking at me. I smiled back, feeling a sense of connection. I knew this was a small part of a much larger world, and I was grateful for the chance to see it. I paid for my gas, and I drove on, the road stretching out before me.

I drove for another hour, the road becoming more desolate. The only sound was the hum of the engine and the wind. I felt a sense of solitude, a peace. I knew this was a time for reflection, a time to think about the things that mattered. I looked out the window, watching the landscape change.

I stopped at a small town, the streets lined with shops. I walked down the main street, looking at the buildings. I felt a sense of nostalgia, a longing for the days when I was a child. I knew this was a place where I had once belonged, and I was happy to be back. I bought a small gift, and I drove home, the road familiar.

I parked the car in front of my house, the door open. I walked inside, the house quiet. I knew this was my home, my sanctuary. I felt a sense of comfort, a peace. I knew I was where I belonged, and I was happy to be home. I closed the door, and I went to bed, the night sky above me.

TABLE IV.

TREATMENT OF MATTOON WATER WITH $\text{Ca}(\text{OH})_2$.

NO.	$\text{Ca}(\text{OH})_2$ c.c.	$\text{Ca}(\text{OH})_2$ as CaCO_3	Alkalinity to Phenolphthalein		Alkalinity to Methyl Orange		Calcium KNaO_4		Magnesium $\text{Mg}_2\text{P}_2\text{O}_7$	
			Filtrate	Corrected for Volume	Filtrate	Corrected for Volume	Corrected c.c.	Corrected for Volume	Corrected from 100 c.c.	Corrected for Volume
			Parts per Million	Parts per Million	Parts per Million	Parts per Million	Milli- grams	Parts per Million	Milli- grams	Parts per Million
1	0	0	0	0	334.	334.	19.3	193.	.0151	157.
2	5	8.5	0	0	349.	352.	19.3	196.	.0131	136.
3	10	17.	0	0	338.	345.	19.3	196.	.0131	136.
4	20	34.	0	0	290.	302.	10.4	110.	.0121	125.
5	30	51.	0	0	253.	268.	10.4	110.	.0121	125.
6	40	68.	0	0	220.	237.	5.6	61.6	.0117	121.
7	50	85.	3	34.	195.	214.	5.6	61.6	.0117	121.
8	60	102.	11	12.	179.	200.	5.8	66.1	.0105	109.
9	70	119.	23	26.	166.	189.	5.8	66.1	.0105	109.
10	80	136.	36	42.	159.	184.	5.4	63.7	.0106	109.
11	90	153.	37	43.	156.	182.	5.4	63.7	.0106	109.
12	100	170.	44	53.	135.	162.	5.8	35.2	.0097	50.
13	110	187.	43	52.	118.	144.	5.8	35.2	.0097	50.
14	120	204.	39	48.	90.	111.	5.9*	36.5	.0025	13.
15	130	221.	44	55.	82.	103.	5.9*	36.5	.0025	13.
16	140	238.	63	80.	98.	125.	13.6	88.4	.0035	18.
17	150	255.	92	119.	130.	169.	13.6	88.4	.0035	18.
18	160	272.	112	148.	146.	192.				

*200 c.c. sample.

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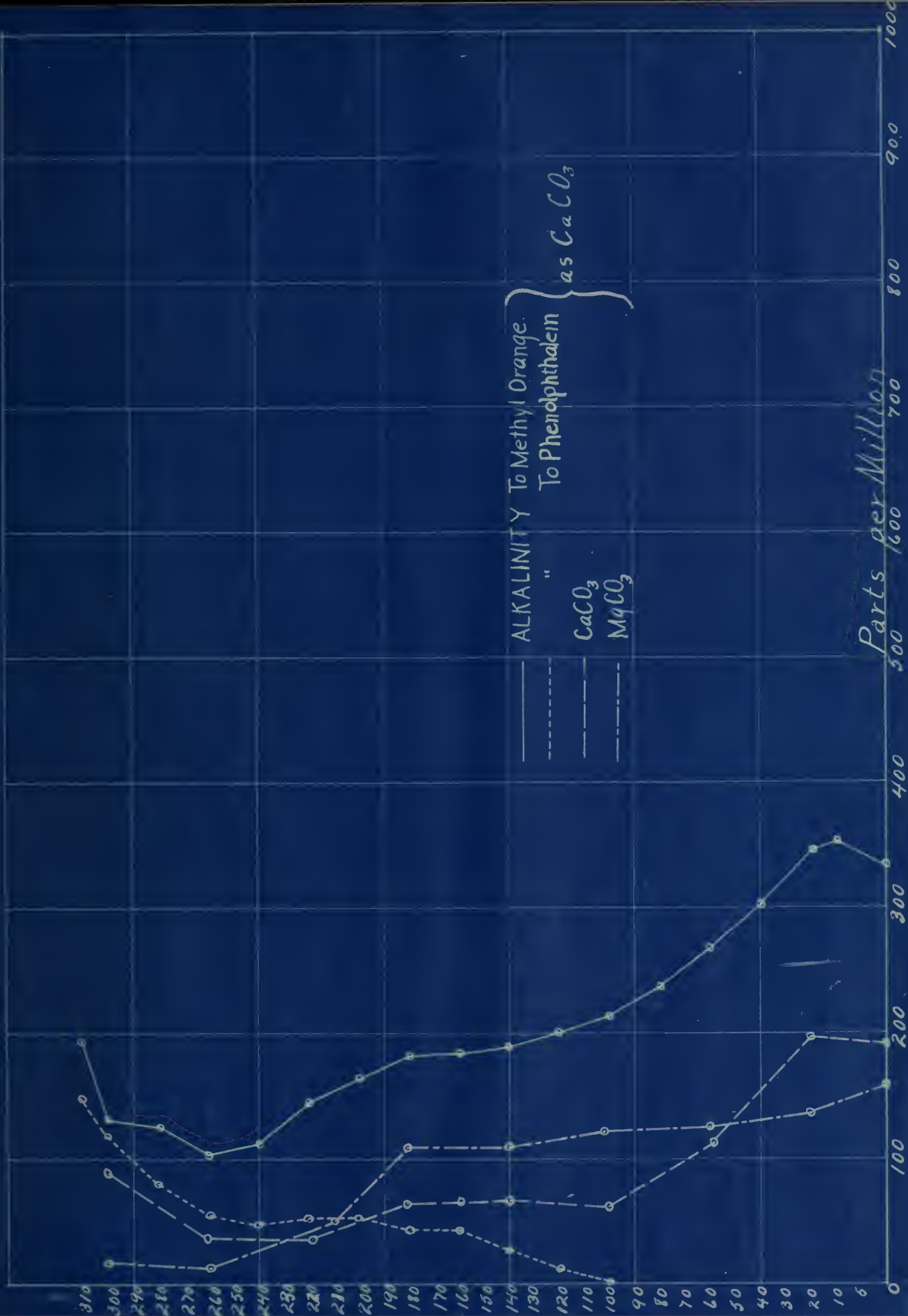
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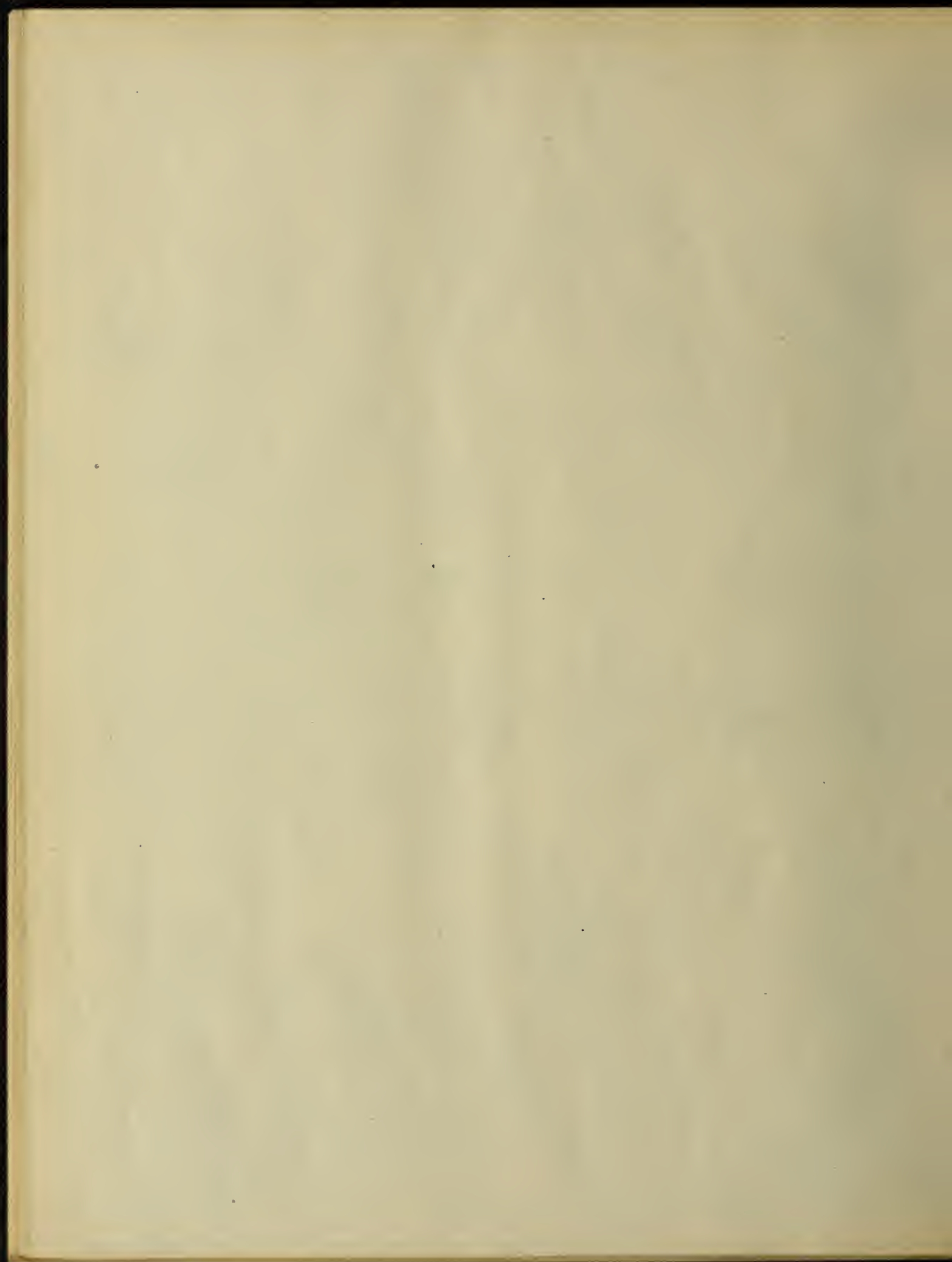
CC. $\text{Ca}(\text{OH})_2$ sol.



ALKALINITY To Methyl Orange.
 " To Phenolphthalein
 CaCO_3
 MgCO_3

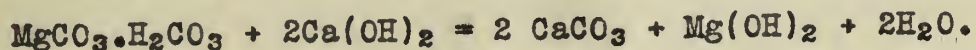
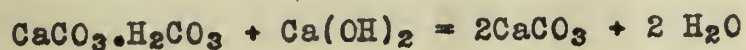
as CaCO_3

Parts per Million



with each other, while the Magnesium content hardly decreases at all. The phenolphthalein alkalinity now appears and increases rapidly. During the third stage the phenolphthalein alkalinity increases rapidly while the Calcium and Magnesium content and methyl orange alkalinity remain almost constant. The action during this stage is probably between the Magnesium bicarbonate and the lime. The Magnesium suddenly decreases rapidly, as does likewise the Calcium content and methyl orange alkalinity and we have reached the fourth stage. In this stage the Magnesium is rapidly precipitated as the hydroxide, insoluble Calcium carbonate being formed at the same time is also precipitated. The Calcium content and methyl orange and phenolphthalein alkalinities now begin to increase showing that an excess of lime has been added.

It is apparent that such a water as this requires only lime treatment and that such treatment is fairly successful. The Calcium is remains fairly completely relatively early in the process, but the Magnesium requires a large amount of lime to remove it to any extent. Reactions involved are:



A water containing large quantities of alkali chlorides and sulfates with alkalaline earth carbonates and sulfates was next treated with lime. The following results were obtained from an analysis of this water some little time previous. This water was obtained from a deep well of the

Kewanee City Water Works, Kewanee, Illinois.

Kewanee City Water.

HYPOTHETICAL COMBINATIONS.

		Parts per Million.
Sodium chloride	NaCl	624.
Sodium sulphate	Na ₂ SO ₄	221.
Magnesium sulphate	MgSO ₄	115.
Magnesium carbonate	MgCO ₃	12.
Calcium carbonate	CaCO ₃	183.
Iron Carbonate	FeCO ₃	3.1

The analytical data are given in the following table while Plate V gives the diagrammatic representation.

In the case of this water the reaction between the lime water and free CO₂ seems to be of short duration and the Calcium begins to decrease immediately. The methyl orange alkalinity begins to decrease rapidly almost immediately. The Magnesium content remains constant. The phenolphthalein alkalinity increases quite slowly and uniformly for a time while the lime is reacting with the CaCO₃.H₂CO₃, then has a sudden, rapid increase. At the same time the Calcium suddenly stops decreasing and remains constant for a time. The Magnesium begins a sudden rapid decrease which shows that the lime is reacting with the MgSO₄ and MgCO₃.H₂CO₃. This decrease is maintained quite uniformly to the end of the series. It is seen that the removal of Magnesium is quite complete. About the time the Magnesium removal is practically complete the methyl orange and phenolphthalein alkalinity and the Calcium

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TABLE V.

TREATMENT OF KEWANEE WATER WITH $\text{Ca}(\text{OH})_2$.

No.	$\text{Ca}(\text{OH})_2$ c.c.	$\text{Ca}(\text{OH})_2$ as CaCO_3	Alkalinity to		Alkalinity to		Calcium		Magnesium	
			Phenolphthalein		Methyl Orange		KMnO_4		Mg_2PaO_7	
			Filtrate	Volume	Filtrate	Volume	c.c. Corrected	for	from Corrected	100 c.c. ed for
			Parts	per	Parts	per	Milli-	Parts	Milli-	Parts
			per	Million	per	Million	grams	per	grams	per
			Million	Million	Million	Million	grams	Million	grams	Million
1	0	0	0	0	245.	245.	16.6	166	.0132	137.
2	5.	8.5	0	0	246.	246.				
3	10.	17.	2.	2.4	245.	245.	13.7	139	.0126	133.
4	20.	34.	2.	2.8	178.	185.				
5	30.	51.	4.	4.2	145.	153.	6.1	64	.0126	138.
6	40.	68.	8.	8.6	124.	133.				
7	50.	85.	23.	25.3	111.	122.	3.2	35	.0109	124.
8	60.	102.	38.	42.4	101.	113.				
9	70.	119.	41.	46.7	83.	95.	2.9	33	.0064	76.
10	80.	136.	41.	46.6	61.	71.				
11	90.	153.	45.	53.1	63.	74.	5.6	66	.0028	34.
12	100.	170.	65.	78.	81.	97.				
13	110.	187.	96.	117.	112.	136.	20.9*	127	.0030*	19.
14	120.	204.	131.	162.	147.	182.				
15	130.	221.	170.	214.	186.	234.	35.3*	222	.0016	10.
16	140.	238.	194.	248.	212.	271.				
17	150.	255.	228.	296.	251.	322.	478	310	.0026	17.5
18	160.	272.	255.	336.	275.	363.				

*200 c.c. sample.

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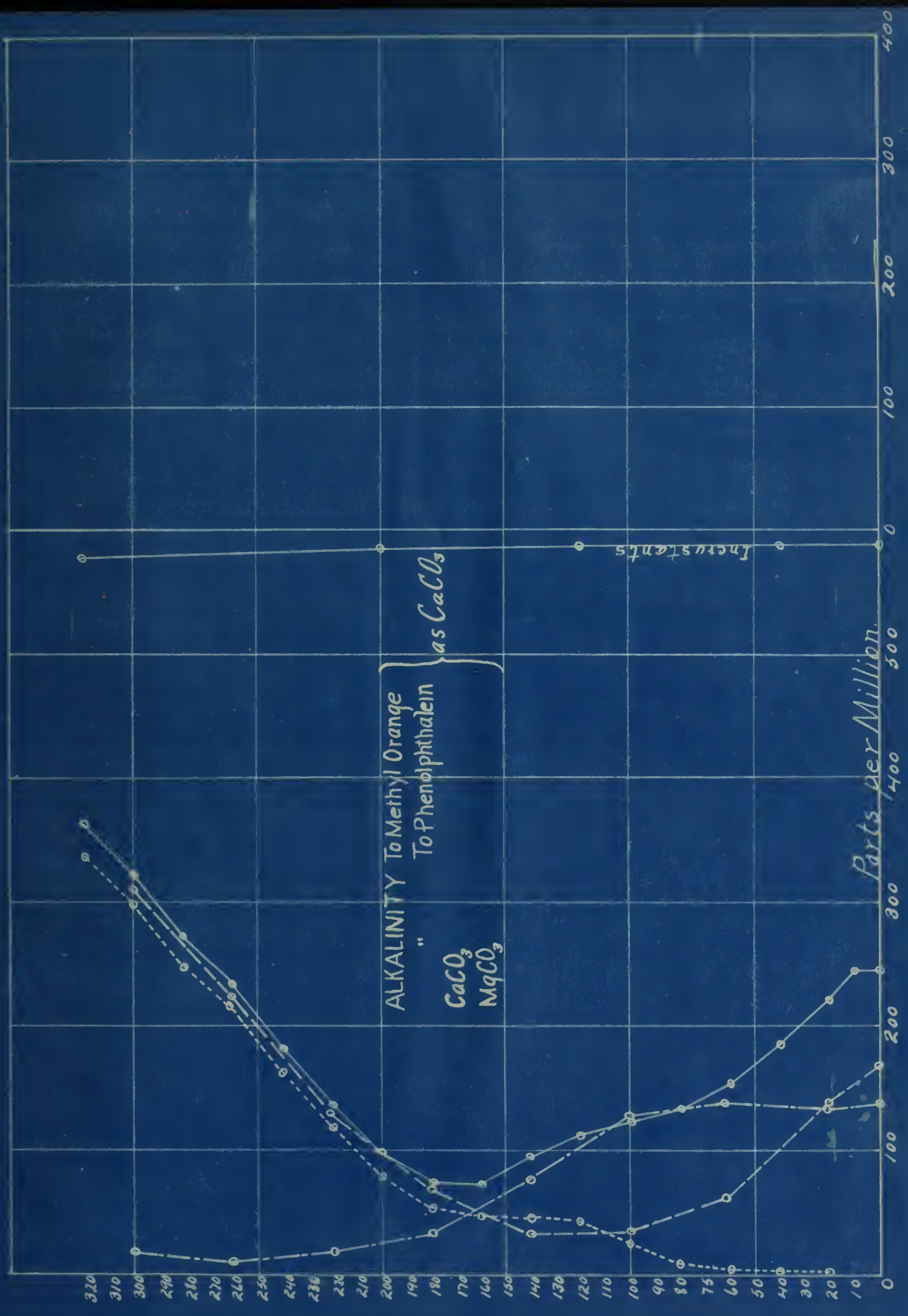
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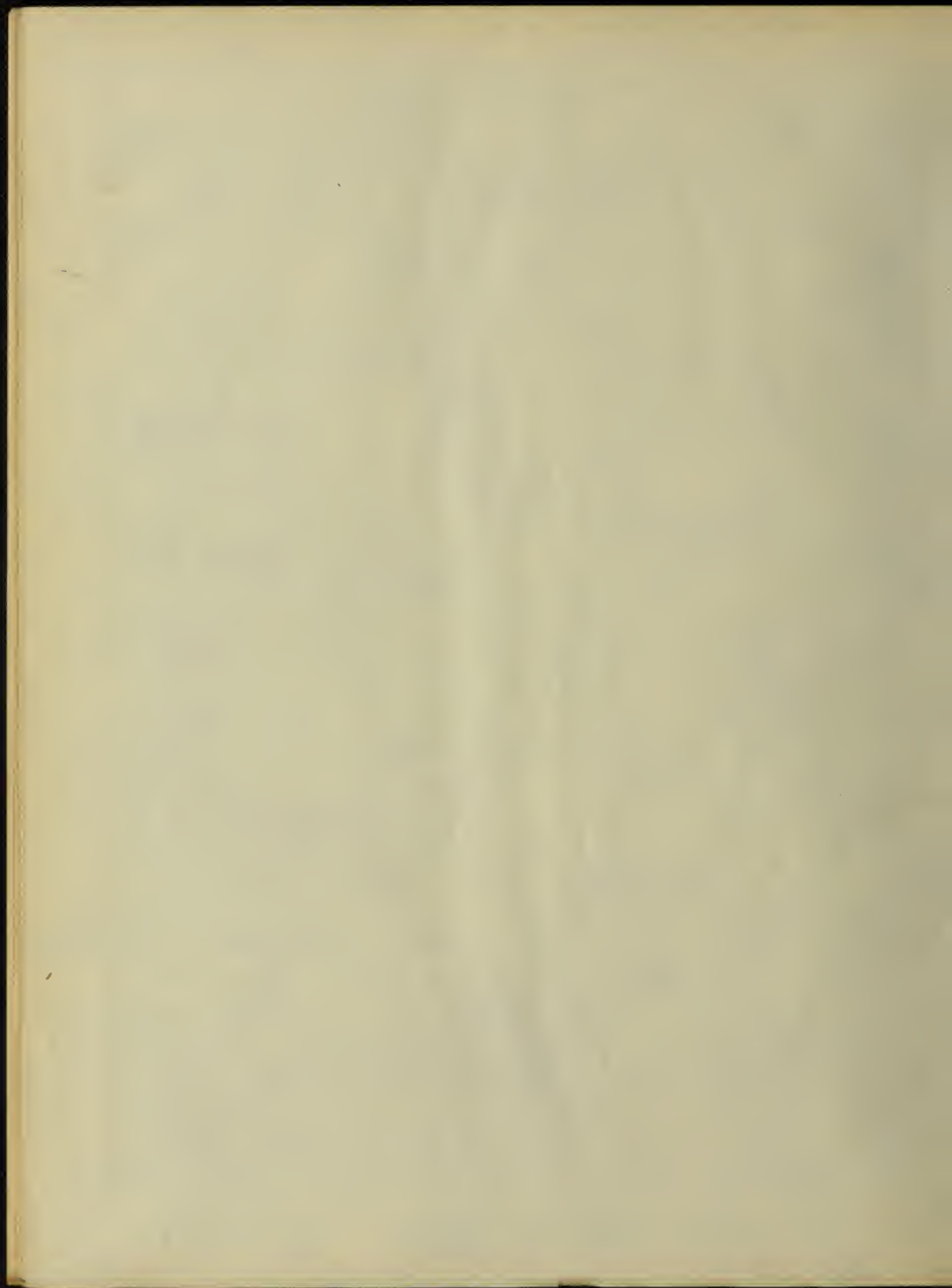
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c.c. $\text{Ca}(\text{OH})_2$ sol.





content begin to imcrease and do so with remarkable uniformity. This merely indicates that an excess of lime has been added. From the results it appears that the treatment of water of this type requires only lime and is very successful. The removal of Calcium and Magnesium salt is quite complete and takes place with the addition of a very moderate amount of lime. The reactions involved have already been given.

A sample of the University water was then treated as above with a solution of $\text{CaH}_4(\text{PO}_4)_2$. ^{precipitation} No ~~reactions~~ took place.

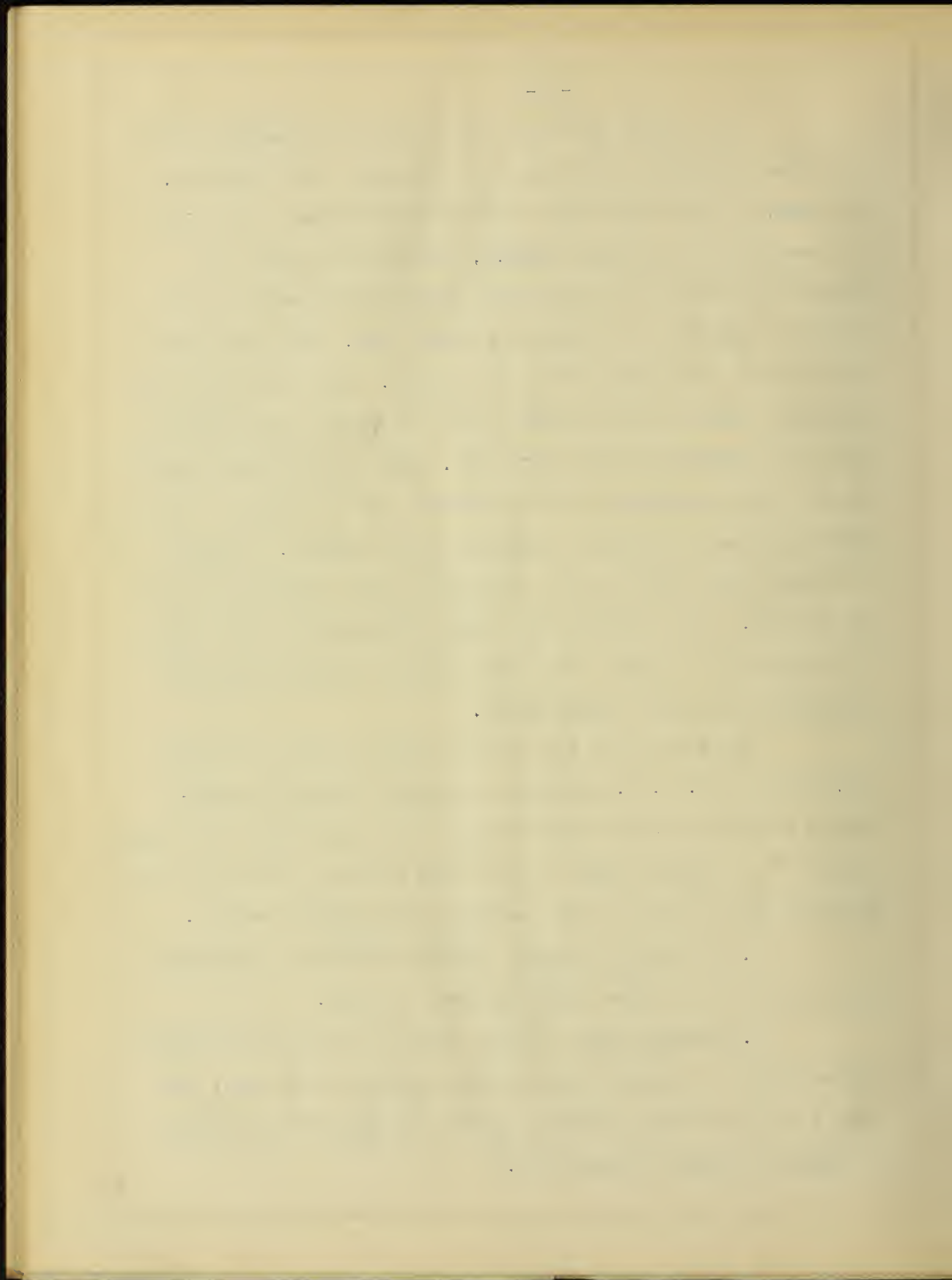
In order to determine the effect of sodium sulfate on the removal of Calcium and Magnesium salts, nineteen samples of University water were taken and the equivalent of 100 parts per Million of sodium sulfate added to each. They were then treated with lime water as in the previous cases, and allowed to stand until the reaction was complete. They were then filtered and the phenolphthalein and methyl orange alkalinities determined. These results were not enough different from those obtained with lime alone to justify the determination of the Calcium and Magnesium content. It would thus seem that sodium sulfate does not interfere to any great extent with the treatment of water with lime. (Stillman J.A.C.S. 25, 732)

Sugar is frequently referred to as a substance used in water treatment. In order to find out if any chemical reactions took place, a few samples of University water were treated with varying amounts of sugar and heated. As was expected ^{precipitation} no ~~reactions~~ took place.

It is well known that heat plays an important part in water softening, when used in conjunction with reagents. To determine just what this effect would be when lime water is used as the softening reagent, a series of samples of University water was treated with different amounts of lime water and heated over night on a water bath. They were then filtered and the alkalinities determined. The results were so irregular that it was concluded that the glass of the bottles had been attacked by the lime water. This view was confirmed by the etched appearance of the bottles and the presence of numerous flakes of silica floating in the samples. Bottles of harder glass could not be obtained so the experiment had to be dropped. It is certain that very interesting results would be obtained by treating water with various reagents and then heating to different temperatures.

The results of experiments along the line of water softening by Mr. J. M. Lindgren and myself warrant the following conclusions, my results dealing with the action of sodium phosphate on various types of water and with the action of lime on alkali and alkaline earth carbonate and sulphate waters.

1. If a water contains sodium bicarbonate, allowance must be made for it when lime treatment is used.
2. In many cases it would probably be more profitable and expedient to remove only calcium carbonate with lime, and resort to some other reagent to remove the Magnesium carbonate or make no attempt to remove it.



3. Lime treatment of waters containing Magnesium sulphate is not satisfactory as an equal number of molecules and a greater weight of Calcium Sulphate remains in the solution.

4. The sodium carbonate treatment for a water containing Magnesium sulphate may be advantageously used only when it is planned to remove the Calcium carbonate and neutralize the incrustants.

5. In either a Magnesium sulphate or a sodium carbonate water it is advisable to consider the relative cost of partial and complete treatment with lime.

6. Treatment of waters containing bicarbonates of the alkalies and alkaline earths with tri-sodium phosphate is quite satisfactory except that there is an increase in the solid residue.

7. Treatment of waters containing sulphate and bicarbonates of the alkaline earths is not very satisfactory, Calcium and Magnesium are incompletely removed.

8. Sodium sulphate does not seem to exert much influence on the removal of Calcium and Magnesium by lime from a water containing bicarbonates of the alkalies and alkaline earths.



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